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The Amino Group in Adenine: MP2 and CCSD(T) Complete Basis Set Limit Calculations of the Planarization Barrier and DFT/B3LYP Study of the Anharmonic Frequencies of Adenine

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The amino group in adenine plays a key role in formation of hydrogen bonds in nucleic acids and in other molecular systems. Thus, the structure of this group is of fundamental importance in the molecular recognition phenomena. Ab initio MP2 and density functional B3LYP methods with various basis sets have been used to calculate the optimized structure and the infrared spectrum of adenine (the N9–H tautomer). Calculations at the MP2 level with larger basis sets tend to decrease the degree of pyramidalization of the C–NH₂ group, whereas the B3LYP method consistently yields the planar or nearly planar structure of adenine. MP2 complete basis set (CBS) limit method with the aug-cc-pVTZ → aug-cc-pVQZ (aTZ → aQZ) extrapolation scheme has predicted very small planarization barrier of adenine, 0.015 kcal/mol, which is in very good agreement with the MP2-predicted planarization barrier of 0.020 kcal/mol, reported by S. Wang and H. F. Schaefer III, *J. Chem. Phys.* **2006**, *124*, 044303. Similar results were obtained in calculations by the coupled cluster CCSD(T) CBS method. Thus, it can be concluded that the amino group in adenine, in the gas phase, is very flexible with a small degree of nonplanarity. Extremely low planarization barrier implies that adenine requires very little energy to conform the structure of the amino group to formation of the complementary hydrogen bonds with other molecules. This fact is very important for base pairing in nucleic acids or other polymers containing adenine residues. The anharmonic frequencies of adenine have been calculated at the B3LYP/6–311++G(d-f,pd) level of theory. The theoretical results show excellent agreement with the available experimental data. The revised assignment of the infrared spectrum of adenine in Ar matrix has been made. The predicted anharmonic frequency of the NH₂ inversion, 181 cm⁻¹, is supported by the experimental data. It is demonstrated that the vibrational frequencies and potential energy distribution (PED) obtained from the B3LYP calculations are more reliable than those obtained at the MP2 level.

1. Introduction

The nonplanarity of the nucleic acid bases is still an intriguing problem. What is the structure of adenine in the gas phase? Is the amino group in adenine coplanar with the molecular rings? These questions seem to still be open in spite of numerous studies. The nonplanarity of the C–NH₂ group is of particularly great importance for investigation of the molecular recognition phenomena involving nucleic acids and other systems containing the adenine residues. The crystal structures of adenine and its derivatives have been determined by high-resolution X-ray and neutron diffraction analyses and are available in the Cambridge Structural Database (CSD).¹ However, there are no direct experimental evidence showing the structure of adenine in the gas-phase. During the recent decades, contradictory results have been reported. The isolated adenine and other nucleic acid bases had been expected to be planar for many years. However, the theoretical studies performed by ab initio second-order Möller–Plesset (MP2) method indicated a distinct pyramidalization of the C–NH₂ group.^{1–11} On the contrary, full geometry optimizations

at the Hartree–Fock^{2,9,12,13} and density functional (DFT) levels of theory^{3,8,14–20} predicted a planar or nearly planar structure of adenine.

In our earlier theoretical studies on aniline, the results obtained at both the B3LYP/6–311++G(df,pd) and MP2/6–311++G(d-f,pd) levels of theory consistently indicated a nonplanar geometry of this molecule in the ground electronic state.²¹ The calculated dihedral angle between the NH₂ plane and the ring plane was equal to 35.5° (B3LYP) and 42.8° (MP2). Both these values were in good agreement with the experimental dihedral angle of 37 ± 2° obtained from the gas-phase microwave studies of aniline.²² Hence, it is puzzling, what is the reason for such discrepancies between the MP2 and DFT results concerning the structure of adenine?

Another problem related with adenine is the tautomerism, which has been thoroughly investigated by many authors.^{9,14,23–29} Calculations performed at different levels of theory consistently indicate that the amino N9–H tautomer has the lowest energy, followed by the N7–H one. Kleinermanns and Plützer²⁸ identified the characteristic frequencies of three N–H stretching vibrations in both the N9–H and N7–H tautomers using resonant two-photon ionization (R2PI) and IR-UV double

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resonance spectra of adenine seeded in a supersonic jet. These authors suggested that the infrared spectra of adenine in the gas phase and in low-temperature inert matrices are a superposition of the IR spectra of the N9–H and N7–H species. Nowak et al.¹⁴ reported the IR spectra of an Ar matrix-isolated adenine and its¹⁵ N isotopomers and concluded that the N9–H tautomer strongly dominates, in the matrix. Only the N(9)–H tautomer was observed by microwave spectroscopy in a supersonic beam experiment.³⁰

Dong and Miller¹¹ determined the vibrational transition moment angles (VTMA) for three bands in the infrared spectrum of adenine cooled in liquid helium nanodroplets. All of the three VTMA values calculated by the MP2 method (for a nonplanar structure) were consistent with the experimental data. In the B3LYP calculations (for a nearly planar optimized structure) one VTMA was much smaller than the experimental value. However, as follows from Figure 2 of ref 11, the band corresponding to this particular VTMA (the asymmetric NH₂ stretching) is very weak and split under perpendicular polarization conditions; thus, the accurate measurement of its integrated IR intensity, and the unequivocal determination of its VTMA, could be difficult. Nevertheless, the authors have concluded that adenine is nonplanar, with the NH₂ group tilted about 20° out-of-plane, as predicted by the MP2 method.

Recently, Wang and Schaefer²⁰ performed a comprehensive theoretical study of the planarization barrier of the amino group in the nucleic acid bases using the ab initio HF and MP2 methods and a series of correlation-consistent basis sets, up to cc-pCVQZ and aug-cc-pVQZ. According to their results, the planarization barrier for adenine is very small, only 0.020 kcal/mol, which is somewhat conflicting with the conclusion made by Dong and Miller.¹¹

The first purpose of this work is to obtain the inversion barrier for the amino group in adenine at the MP2 and coupled cluster CCSD(T) levels of theory using various basis sets for extrapolation to the complete basis set (CBS) limit.³¹ The second purpose of this work is to provide the clear-cut assignment of the infrared spectrum of adenine in an Ar matrix on the basis of the potential energy distribution (PED) and the anharmonic frequencies calculated at the B3LYP/6–311++G(df,pd) level.

2. Theoretical Methods

Full geometry optimization of adenine was followed by calculations of the vibrational harmonic frequencies and infrared intensities, at each level of theory. The Becke's three-parameter density functional (DFT/B3LYP)^{32–34} and the MP2 method³⁵ with various basis sets have been used. The basis sets included the valence double- ζ and valence triple- ζ , augmented by polarization and diffuse functions for all atoms.^{36,37} A series of correlation-consistent polarized valence basis sets, cc-pVXZ (X = D, T, and Q) have also been employed. The aug-cc-pVXZ basis was constructed by augmenting the cc-pVXZ set with diffuse functions.^{38,39}

The anharmonic frequencies of adenine were calculated at the B3LYP/6–311++G(df,pd) level of theory using a second-order perturbative treatment based on quadratic, cubic, and semidiagonal quartic force constants. The whole algorithm elaborated by Barone^{40,41} has been implemented in the Gaussian package.⁴² To perform the normal coordinate analysis, we have used the nonredundant set of 39 internal coordinates, as defined by Nowak et al.,¹³ and followed the formulas reported by Fogarasi and Pulay.⁴³ The procedure was similar to that described in our earlier studies.^{44,45} The potential energy distribution (PED) was calculated for all normal modes of adenine, at each level of theory.

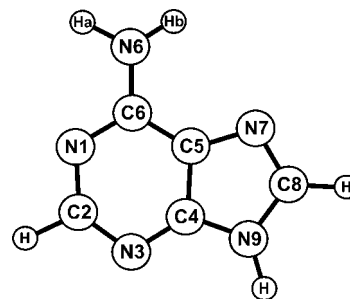


Figure 1. Molecular structure of adenine and the numbering of atoms.

The planarization barrier was determined as the difference between the total energies of the nonplanar and planar forms of the adenine molecule, obtained by the complete basis set (CBS) limit calculations at the MP2 or CCSD(T) levels of theory. The CBS limit energies were derived by the separate extrapolation of the Hartree–Fock energy and the MP2 or CCSD(T) correlation energy using various correlation-consistent basis sets ranging from double- ζ to quadruple- ζ quality.^{38,39} The two-point extrapolation scheme of Halkier et al.^{46,47} has been employed. In this work, the cc-pVXZ and aug-cc-pVXZ basis sets are abbreviated as XZ and aXZ, respectively (where, X = D, T, and Q).

All these calculations have been performed by GAUSSIAN 03,⁴² MOLPRO 2006,⁴⁸ and TURBOMOLE 5.10 packages.⁴⁹

3. Results and Discussion

3.1. Structural Parameters. Figure 1 shows the structure of adenine with the numbering of atoms. According to the results obtained with all theoretical methods, both the five- and six-membered rings in adenine are planar and coplanar, which is in agreement with the experimental data.^{1,50}

Table 1 shows the optimized C6–N6 and N6–H atom distances and bond angles around the amino nitrogen atom N6 in adenine. The experimentally determined median value for the C6–N6 bond length is 1.336 Å (obtained from the high-resolution X-ray and neutron diffraction studies of adenine and its derivatives in the solid state).¹ It should be noticed that the corresponding C–N bond length in the nonplanar aniline is significantly longer, 1.402 ± 0.002 Å (from the gas-phase microwave studies).²² In our earlier theoretical study on aniline,²¹ both the B3LYP and MP2 methods yielded similar C–N atom distances, 1.395 and 1.402 Å, respectively, which are in very good agreement with experiment.

As is seen in Table 1, all the theoretical methods overestimate the experimental C6–N6 bond length in adenine. However, the results from the B3LYP calculations for planar adenine show much better agreement with experiment, in comparison with the results obtained by the MP2 method for the nonplanar structure. When the structure of adenine is constrained to planarity in the MP2 calculations, the agreement between the experimental and theoretical C6–N6 bond length improves, for example, the C6–N6 atom distance decreases from 1.358 Å (nonplanar) to 1.349 Å (constraint-planar) in the calculations at the MP2/cc-pVTZ level of theory. As follows from comparison of the B3LYP results, an increase in the size of the basis set improves agreement with experiment; the C6–N6 atom distance calculated with all the triple- ζ basis sets is shorter and closer to the experimental value than that obtained with the double- ζ basis set. The opposite effect is noted for the MP2 calculations, the C6–N6 bond length predicted by a small basis set, 6–31G(d) shows better agreement with the experiment that

TABLE 1: The C–N and N–H Bond Lengths (in Angstroms) and Bond Angles (in Degrees) of the C–NH₂ Group in Adenine Optimized by the B3LYP and MP2 Methods Using Various Basis Sets

	C6–N6	N6–H	C6–N6–Ha	C6–N6–Hb	Ha–N6–Hb	sum ^a
B3LYP/6–31G(d)	1.358 (0.022) ^b	1.010	117.5	118.8	118.7	355.0
B3LYP/6–311G(d)	1.351 (0.015)	1.005	119.1	120.5	120.3	359.9
B3LYP/6–311G(df)	1.348 (0.012)	1.003	119.0	120.3	120.6	359.9
B3LYP/6–311G(d,p)	1.351 (0.015)	1.005	119.0	120.2	120.7	359.9
B3LYP/6–311G(df,pd)	1.349 (0.013)	1.004	119.0	120.5	120.5	360.0
B3LYP/6–311+G(d,p)	1.353 (0.017)	1.006	119.1	120.4	120.4	359.9
B3LYP/6–311++G(d,p)	1.353 (0.017)	1.006	119.1	120.4	120.4	359.9
B3LYP/6–311++G(df,pd)	1.350 (0.014)	1.006	119.1	120.5	120.4	360.0
MP2/6–31G(d)	1.364 (0.028)	1.012	115.7	116.8	116.9	349.4
MP2/6–311+G(d,p)	1.366 (0.030)	1.010	115.7	116.8	116.8	349.3
MP2/6–311++G(df,pd)	1.362 (0.026)	1.009	115.8	116.7	117.0	349.5
MP2/cc-pVDZ	1.371 (0.035)	1.016	114.4	115.2	115.7	345.3
MP2/cc-pVTZ	1.358 (0.022)	1.005	116.3	117.1	117.9	351.3
MP2/cc-pVQZ	1.354 (0.018)	1.003	116.9	117.8	118.5	353.2
MP2/aug-cc-pVDZ	1.368 (0.032)	1.013	116.7	117.6	118.1	352.4
MP2/aug-cc-pVTZ	1.357 (0.021)	1.006	117.1	118.0	118.6	353.7
constrained planar						
MP2/cc-pVDZ	1.356 (0.020)	1.011	119.1	119.9	121.0	360.0
MP2/cc-pVTZ	1.349 (0.013)	1.002	119.1	119.9	121.0	360.0

^a The sum of the three angles around the N6 atom. ^b In parentheses are shown the differences between the theoretical (gas phase) and experimental (1.336 Å, solid state) values.

that obtained at the MP2/cc-pVDZ level. Regarding the B3LYP results, a further enlargement of the triple- ζ basis set by addition of various polarization and diffuse functions has very little effect on the calculated C6–N6 bond length.

The differences between the calculated N6–H6a and N6–H6b distances are smaller than 0.001 Å, therefore, we denote both of them as N6–H (an average is given in Table 1). Unfortunately, there are no available experimental data for the N–H bond length in adenine. In aniline, the experimentally obtained N–H distance is 1.001 Å.²²

The three bond angles around the amino nitrogen atom N6 are also listed in Table 1. In all MP2 calculations, the two C6–N6–H angles are smaller than those predicted by the B3LYP method. The last column of Table 1 shows the sum of three angles, which can be used as a measure of the degree of pyramidalization of the C–NH₂ group (for the perfectly planar structure the sum equals to 360.0°). As follows from these results, the B3LYP method with all the basis sets (except for the smallest one) predicts the planar structure of the C–NH₂ group (the sum equals to 359.9 or 360°). In contrast, all calculations by the MP2 method predict the pyramidalized structure; however, when a larger basis set is used, the deviation from planarity decreases. For example, the difference (360.0° – sum) is equal to 10.6° with the 6–31G(d) basis set, and it decreases to 6.8° with the cc-pVQZ basis set. Geometry optimization at the MP2/aug-cc-pVTZ level leads to a further decrease of this difference to 6.3°.

The optimized dihedral angles involving the amino group in adenine are compared in Table 2. The MP2 results show a strong basis set dependence. It is noticed that calculations performed with the basis sets augmented by diffuse functions tend to decrease the degree of pyramidalization of the C–NH₂ group. For example, the N1–C6–N6–Ha angle decreases from 17.0° (cc-pVTZ) to 14.8° (aug-cc-pVTZ). The Ha–N6–Hb–C6 dihedral angle (the second column in Table 2) for a perfectly planar structure should be equal to 180.0°. The MP2 method yields a large deviation from this value, ranging from 43° (cc-pVDZ) to 28.4° (aug-cc-pVTZ basis set).

3.2. Rotational constants. The rotational constants calculated at various levels of theory, and those determined by microwave spectroscopic study,³⁰ are compared in Table 3.

TABLE 2: The Amino-group-related Dihedral Angles (in Degrees) in Adenine Optimized by the B3LYP and MP2 Methods Using Various Basis Sets

	Ha–N6– Hb–C6	N6–C6– N1–C5	N1–C6– N6–Ha	N1–C6– N6–Hb
B3LYP/6–31G(d)	154.7	178.7	12.8	167.4
B3LYP/6–311G(d)	178.7	179.9	0.6	179.4
B3LYP/6–311G(df)	179.8	180.0	0.1	179.9
B3LYP/6–311G(d,p)	178.7	179.9	0.6	179.4
B3LYP/6–311G(df,pd)	180.0	180.0	0.0	180.0
B3LYP/6–311+G(d,p)	178.8	179.9	0.4	179.6
B3LYP/6–311++G(d,p)	176.4	179.8	1.8	178.3
B3LYP/6–311++G(df,pd)	179.3	180.0	0.3	179.7
MP2/6–31G(d)	143.1	176.8	18.7	162.2
MP2/6–311+G(d,p)	143.2	176.5	19.1	162.4
MP2/6–311++G(df,pd)	143.6	176.2	19.0	163.0
MP2/cc-pVDZ	137.0	177.3	21.7	159.3
MP2/cc-pVTZ	146.5	178.0	17.0	164.1
MP2/cc-pVQZ	150.0	178.3	15.3	166.0
MP2/aug-cc-pVDZ	148.8	177.8	16.1	165.1
MP2/aug-cc-pVTZ	151.6	178.2	14.8	166.6

The calculated rms values vary in the range between 4 and 21 MHz. The best accuracy (4 MHz) has been obtained for both the planar structure, calculated by the B3LYP/6–311+G(d,p) method, and the nonplanar structure, obtained at the MP2/6–311++G(df,pd) level. This indicates that pyramidalization of the C–NH₂ group has a very small influence on the calculated rotational constants.

Thus, the rotational constants cannot be used to conclude definitely whether the molecule is planar or not.

3.3. Vibrational Spectra and Their Assignment. The infrared spectra of adenine isolated in low-temperature Ar, Ne, and N₂ matrices were thoroughly studied by Nowak and co-workers,^{13,14} and earlier by Stepanian et al.⁵³ The gas-phase IR spectra of adenine were reported by Colarusso et al.⁵¹ Vibrational frequencies of adenine were previously calculated at various levels of theory, such as ab initio HF/4–21G,¹² HF/6–31G(d,p),¹³ density functional B3LYP/6–31G(d,p),¹⁴ BP86/6–311G,⁵⁴ DFT-GGA with ultrasoft pseudopotentials,¹⁸ B3LYP/6–31G(d) combined with SQM method,^{8,9} GGA/DNP approach,⁵⁵ and the ab initio MP2 methods.^{10,56} However, despite

TABLE 3: Experimental and Calculated Rotational Constants of Adenine

	A ^a	B	C	rms ^b
exp. ^c	2371.873(4)	1573.3565(8)	946.2576(4)	
B3LYP/6-31G(d)	2368.21	1565.76	942.80	5
B3LYP/6-311+G(d,p)	2377.23	1568.47	944.98	4
B3LYP/6-311++ G(df,pd)	2384.09	1572.49	947.52	7
MP2/6-31G(d)	2356.38	1572.03	943.44	9
MP2/6-311+G(d,p)	2357.00	1569.91	942.80	9
MP2/6-311++ G(df,pd)	2370.92	1579.23	948.35	4
MP2/cc-pVDZ	2339.43	1561.48	937.10	21
MP2/cc-pVTZ	2373.19	1582.54	949.82	6
MP2/cc-pVQZ	2382.18	1586.46	952.58	10
constrained planar				
MP2/cc-pVDZ	2342.47	1563.10	937.51	19
MP2/cc-pVTZ	2375.01	1583.45	950.04	6
MP2/cc-pVQZ	2383.56	1587.16	952.75	11

^a Rotational constants A, B, C are reported in megahertz.

^b Root-mean-square deviation. ^c From ref 30.

these numerous studies, the assignment of some bands is contradictory, and the origin of a splitting of some bands in low-temperature matrices is still unclear. Nowak et al.^{13,14} claimed that the splitting was caused by matrix effects, but the other authors²⁸ suggested that two adenine tautomers, N9-H and N7-H, were present in matrices.

To elucidate these ambiguities, we have calculated the anharmonic (and the corresponding harmonic) vibrational frequencies, infrared intensities, and potential energy distribution (PED) using the B3LYP method with the 6-311++G(df,pd) basis set. We have shown in our earlier works^{21,57,58} that this level of theory predicts very well the infrared spectra of molecules. The theoretical results obtained in this work, and the available experimental data, are summarized in Table 4.

As is seen from this table, the calculated anharmonic frequencies are in excellent agreement with experiment.^{13,14,28,51} This has enabled us to provide a clear-cut vibrational assignment for the N9-H tautomer. Several bands have been reassigned on the basis of the new theoretical data.

The three calculated anharmonic N-H stretching frequencies, at 3539, 3497, and 3432 cm⁻¹, match to the experimental frequencies at 3569, 3508, and 3452 cm⁻¹, determined for the N9-H tautomer of adenine in a supersonic jet.²⁸ They show also very good agreement with the bands observed at 3552, 3501, and 3434 cm⁻¹, in the gas-phase emission spectrum of adenine.⁵¹ It should be noticed that in the IR spectrum of adenine isolated in an argon matrix, in the region from 3430 to 3570 cm⁻¹, the absorption bands show a very complicated pattern with 13 "maxima";¹⁴ therefore, their detailed assignment is difficult.

The C8-H and C2-H stretching vibrations of adenine in an Ar matrix were previously assigned at 3057 and 3041 cm⁻¹, respectively,¹⁴ whereas in the gas phase spectrum, the former vibration was attributed to the band at 3061 cm⁻¹.⁵¹ According to our results, these assignments are incorrect. The calculated anharmonic frequency of the ν (C8-H) vibration (Q4 mode) is 3102 cm⁻¹, whereas the predicted infrared intensity is almost zero; therefore, this mode should not be observed in the IR spectrum of the N9-H tautomer. Thus, that the band at 3057 cm⁻¹ in Ar matrix (3061 cm⁻¹ in the gas-phase) is assigned to the ν (C2-H) stretching vibration. A weak band at 3041 cm⁻¹ can be attributed to the N7-H tautomer. The infrared spectra of adenine in Ar or Ne matrices show many split or closely

lying bands. This may indicate that not only the N9-H, but also the N7-H tautomer is present in low-temperature matrices.

The band at 1017 cm⁻¹ in Ar matrix (and 1018 cm⁻¹ in the gas-phase) corresponds to the anharmonic frequency (1018 cm⁻¹) calculated for the Q20 mode. It is interesting to note that the anharmonic frequency of this mode is slightly higher than the corresponding harmonic one. According to the calculated PED, mode Q20 has the predominant (48%) contribution from the NH₂ rocking vibration coupled with the N₁-C₆ stretching vibration (28%). The B3LYP method predicts very well the frequency of this mode, whereas the DFT-GGA approach with ultrasoft pseudopotential and a plane-wave basis¹⁸ underestimates this frequency by about 95 cm⁻¹, in comparison to experiment.

Nowak et al.¹⁴ observed a distinct doublet at 591, 583 cm⁻¹ in an argon matrix. Xue et al.⁸ assigned these bands to the NH₂ torsion (twisting) vibration, on the basis of the SQM calculations, whereas Santamaria et al.⁵⁴ assigned them to the NH₂ rocking vibration. According to our results, these assignments are incorrect. The NH₂ twisting vibration has a predominant contribution (79%) to the mode Q34, which is assigned at 503 cm⁻¹ in argon matrix, in agreement with Nowak et al.,¹⁴ whereas the NH₂ rocking vibration contributes to two bands observed at 1229 cm⁻¹ (Q17 mode) and 1017 cm⁻¹ (Q20 mode). It should be emphasized that our calculations do not predict any theoretical frequencies corresponding to a doublet around 590 cm⁻¹, observed in an argon matrix.^{13,14} Thus, we agree with an earlier suggestion made by Nowak et al.¹⁴ that this doublet does not correspond to any fundamental transition, and most probably it arises from higher overtones of the NH₂ inversion mode.

Substantial discrepancy has been found between the theoretical frequencies of the NH₂ inversion mode (called also the NH₂ wagging vibration), obtained at various levels of theory. It has been calculated at 93 and 438 cm⁻¹ by the HF/6-31G(d,p)¹³ and the MP2/6-31G(d) methods,⁵⁶ respectively, whereas the DFT-GGA method with ultrasoft pseudopotentials predicted its frequency at 156 cm⁻¹.¹⁸

Nowak et al.,¹⁴ in the matrix isolation IR spectrum of adenine, assigned the band at 242 cm⁻¹ to the NH₂ inversion vibration. According to our results, this assignment should be revised. As follows from Table 4, mode Q38 has the largest contribution (71%) from the NH₂ inversion vibration. The calculated anharmonic frequency of this mode is 181 cm⁻¹, and the predicted infrared intensity is quite large. It is noticed that the band at 244 cm⁻¹ is very weak, in the gas-phase spectrum of adenine.⁵¹ Thus, we have assigned the NH₂ inversion vibration (mode Q38) to the band at 184 cm⁻¹, detected by neutron inelastic scattering (NIS) spectroscopy.⁵² It should be emphasized that of all the bands, in the spectral region below 400 cm⁻¹, this particular band shows the largest downward shift (of 30 cm⁻¹) upon N-deuteration,⁵² which confirms our assignment. In the gas-phase spectrum of adenine, the band at 162 cm⁻¹ may originate from the NH₂ inversion mode; however, this assignment is less certain. As is seen in Table 4, there is no theoretically predicted counterpart for the band observed at 242 cm⁻¹ in Ar matrix. Therefore, this band may not correspond to any fundamental vibration of the N9-H tautomer of adenine.

According to our results, mode Q37 is a coupled vibration involving a "butterfly" motion of the adenine rings (54%), NH₂ inversion (21%), and the torsion vibration of the 6-membered ring (18%). The calculated anharmonic frequency of this mode, 209 cm⁻¹, corresponds very well to the band observed at 214 cm⁻¹, in Ar matrix,^{13,14} and to the band at 208 cm⁻¹, in the gas-phase.⁵¹

TABLE 4: Comparison of the Experimental Matrix and Gas Phase Frequencies (ν , in cm^{-1}), Calculated Anharmonic and Harmonic Frequencies (ω^{anhar} and ω^{har} , in cm^{-1}), Calculated IR Intensities (A , km/mol), and Potential Energy Distribution (PED) for Adenine (N9–H)^a

	exp.			B3LYP/6–311++G(df,pd)			PED (%) ^d
	ν^b	I_{rel}^b	ν^c	ω^{anhar}	ω^{har}	A	
Q1	3569 ^e		3552 m	3539	3747	64	$\nu_{\text{asym}} \text{NH}_2(100)$
Q2	3508 ^e		3501 s	3497	3656	87	$\nu(\text{N}_9\text{--H})(100)$
Q3	3452 ^e		3434 s	3432	3614	100	$\nu_{\text{sym}} \text{NH}_2(100)$
Q4 ^f				3102	3241	0	$\nu(\text{C}_8\text{--H})(99)$
Q5 ^f	3057	6	3061 m	3049	3167	18	$\nu(\text{C}_2\text{--H})(100)$
	3041	3					
	1639						
Q6	1633	447	1625 vs	1616	1655	650	$\delta_{\text{sciss}} \text{NH}_2(31)$, $\nu(\text{C}_5\text{--C}_6)(+21)$, $\nu(\text{C}_6\text{--N}_6)(-19)$
Q7	1612	219		1591	1633	117	$\nu(\text{N}_3\text{--C}_4)(-27)$, $\nu(\text{C}_5\text{--C}_6)(+10)$
Q8	1599	49		1577	1608	13	$\delta_{\text{sciss}} \text{NH}_2(50)$, $\nu(\text{C}_4\text{--C}_5)(+13)$, $\nu(\text{C}_5\text{--C}_6)(-10)$
Q9	1482	11		1481	1516	8	$\nu(\text{N}_7\text{--C}_8)(-45)$, $\delta\text{C}_8\text{H}(+21)$
Q10	1474	71	1468 s	1466	1503	84	$\nu(\text{N}_1\text{--C}_6)(+25)$, $\delta\text{C}_2\text{H}(+23)$, $\nu(\text{C}_2\text{--N}_3)(-13)$, $\nu(\text{C}_6\text{--N}_6)(-13)$
Q11	1419	49	1415 s	1406	1435	18	$\nu(\text{C}_4\text{--C}_5)(+25)$, $\nu(\text{C}_4\text{--N}_9)(-15)$, $\delta\text{C}_2\text{H}(-15)$
Q12	1389	45		1376	1414	14	$\delta\text{N}_9\text{H}(-26)$, $\delta\text{C}_2\text{H}(+22)$, $\nu(\text{C}_4\text{--N}_6)(-16)$, $\nu(\text{C}_8\text{--N}_9)(+12)$
Q13 ^f	1345	21	1346 m	1338	1366	23	$\delta\text{C}_2\text{H}(+19)$, $\nu(\text{C}_8\text{--N}_9)(-14)$, $\delta\text{C}_8\text{H}(-11)$, $\nu(\text{C}_6\text{--N}_6)(+11)$
	1334	7					
Q14	1328	40	1326 s	1325	1357	43	$\nu(\text{N}_1\text{--C}_2)(+30)$, $\nu(\text{C}_5\text{--N}_7)(+22)$, $\nu(\text{C}_4\text{--C}_5)(-10)$
Q15	1290	68	1280 s	1291	1326	74	$\nu(\text{C}_2\text{--N}_3)(+48)$, $\nu(\text{N}_1\text{--C}_2)(-14)$
	1246	9					
Q16	1240	28		1243	1270	29	$\delta\text{C}_8\text{H}(+35)$, $\nu(\text{N}_7\text{--C}_8)(+17)$, $\delta\text{N}_9\text{H}(+11)$
Q17	1229	13	1234 s	1230	1243	15	$\delta_{\text{rock}} \text{NH}_2(25)$, $\nu(\text{C}_5\text{--N}_7)(-25)$, $\nu(\text{C}_2\text{--N}_3)(+10)$
	1133	7					
Q18	1127	6	1126 w	1125	1145	22	$\nu(\text{C}_4\text{--N}_9)(-20)$, $\delta\text{r}2(14)$, $\nu(\text{C}_6\text{--N}_6)(+10)$
Q19	1061	13	1053 w	1054	1081	22	$\nu(\text{C}_8\text{--N}_9)(+57)$, $\delta\text{N}_9\text{H}(+31)$
	1032	27					
Q20 ^f	1017	4	1018 m	1018	1008	5	$\delta_{\text{rock}} \text{NH}_2(48)$, $\nu(\text{N}_1\text{--C}_6)(+28)$
	1005	9					
Q21	958	3		969	979	4	$\gamma\text{C}_2\text{H}(100)$
Q22	927	13	926 vw	931	945	15	$\delta\text{r}1(74)$, $\nu(\text{C}_4\text{--C}_5)(+11)$
Q23	887	8		885	900	12	$\delta\text{R}1(49)$, $\delta\text{R}3(15)$
Q24	848	6	847 w	846	854	8	$\gamma\text{C}_8\text{H}(98)$
Q25	802	9	801 w	811	810	12	$\tau\text{R}1(50)$, $\tau\text{r}1(24)$, $\gamma\text{C}_6\text{N}_6(+22)$
Q26	717	5		717	726	2	$\nu(\text{N}_3\text{--C}_4)(+21)$, $\nu(\text{C}_5\text{--N}_7)(+11)$, $\nu(\text{C}_4\text{--N}_9)(+10)$
Q27 ^f	678	2		677	686	1	$\gamma\text{C}_6\text{N}_6(+47)$, $\tau\text{r}1(24)$, $\tau\text{Rr}(13)$
Q28	655	6		655	669	7	$\tau\text{r}2(83)$
Q29	610	5		610	619	1	$\delta\text{r}2(35)$, $\nu(\text{C}_5\text{--C}_6)(+23)$, $\delta\text{R}3(22)$
	591/583	99					
Q30 ^f	566	46	563 w	570	579	69	$\gamma\text{N}_9\text{H}(+29)$, $\tau\text{R}1(20)$, $\tau\text{R}2(16)$, $\tau\text{r}1(15)$
Q31 ^f				529	532	2	$\delta\text{R}2(73)$
Q32 ^f	513	92	515 w	518	532	54	$\gamma\text{N}_9\text{H}(62)$, $\text{twist NH}_2(17)$
Q33 ^f				516	521	5	$\delta\text{R}3(30)$, $\delta\text{C}_6\text{N}_6(25)$, $\nu(\text{C}_4\text{--N}_9)(-12)$
Q34 ^f	503	4	506 m	491	544	7	$\text{twist NH}_2(79)$, $\gamma\text{N}_9\text{H}(10)$
Q35				299	300	0	$\tau\text{R}2(42)$, $\tau\text{r}1(23)$, $\tau\text{R}3(17)$, $\tau\text{Rr}(10)$
Q36	276	12	270 m	276	277	12	$\delta\text{C}_6\text{N}_6(53)$, $\delta\text{R}3(15)$, $\delta\text{r}2(10)$
	242	66	244 vw				
Q37 ^f	214	75	208 m	209	223	25	$\tau\text{Rr}(54)$, $\text{inv NH}_2(21)$, $\tau\text{R}3(18)$
Q38 ^f	184 ^g		162 m	181	180	178	$\text{inv NH}_2(71)$, $\tau\text{Rr}(16)$, $\tau\text{R}2(10)$
Q39				139	156	17	$\tau\text{R}3(45)$, $\gamma\text{C}_6\text{N}_6(18)$, $\tau\text{r}1(14)$, $\tau\text{R}2(10)$

^a Calculations have been performed at the B3LYP/6–311++G(df,pd) level. ^b Argon matrix IR data from ref 14 or as indicated otherwise. ^c From gas-phase data in ref 51. ^d Abbreviations: ν , stretching; δ , in-plane bending; γ , out-of-plane bending; τ , torsional; sciss, scissoring; rock, rocking; inv, inversion (wagging) vibration; R1, R2, and R3 are deformations of the 6-membered ring; r1 and r2 are deformations of the 5-membered ring; τRr , butterfly motion of purine rings. The + sign denotes the in-phase motion, the – sign denotes the out-of-phase motion. ^e From IR-UV data in ref 28. ^f Reassigned mode or different PED than that reported in literature. ^g From NIS data in ref 52.

Mode Q36 has the predominant contribution (53%) from the in-plane bending vibration of the $\text{C}_6\text{--N}_6$ bond. It should be noticed that the calculated anharmonic frequency of this vibration, 276 cm^{-1} , reproduces the experimental frequency of 276 cm^{-1} , observed for adenine in Ar matrix.¹⁴ The lowest calculated anharmonic frequency is 139 cm^{-1} , but the corresponding vibration has not yet been observed experimentally.

We have also calculated the infrared spectra of adenine by the MP2 method using several basis sets. The rigorous normal coordinate analysis has been performed at each level of theory (the results are listed in the Supporting Information). Examina-

tion of the calculated PEDs has revealed significant discrepancies between the character of the normal modes obtained by the MP2 and B3LYP methods. For instance, the mode containing NH_2 inversion has been predicted at 388, 462, and 501 cm^{-1} , in calculations at the MP2/cc-pVTZ, MP2/6–31G(d), and MP2/6–311++G(df,pd) levels of theory, respectively. Moreover, according to PEDs obtained in the MP2 calculations, there is no band assignable to NH_2 vibration in the frequency region below 380 cm^{-1} . These results are contradictory to the experimental data obtained for the N-deuterated adenine, which prove that the bands at 214 cm^{-1} ^{13,14} and 184 cm^{-1} ⁵² involve

TABLE 5: Planarization Barrier for Adenine Calculated at Different Levels of Theory

	MP2 ^a	MP2/CBS ^b		CCSD(T)/ CBS ^b
	aQZ	aDZ → aTZ ^c	aTZ → aQZ ^c	aDZ → aTZ ^c
kcal/mol	0.020	0.098	0.015	0.125
cm ⁻¹	7	34	5	44

^a From ref 20, aQZ denotes the aug-cc-pVQZ basis set. ^b This work, the MP2 and CCSD(T) complete basis set limit planarization energy. ^c The arrow means extrapolations from the aug-cc-pVDZ to aug-cc-pVTZ or from the aug-cc-pVTZ to aug-cc-pVQZ basis sets.

a large contribution from the NH₂ out-of-plane vibration. It is remarkable that the DFT/B3LYP method predicts the frequencies of adenine in excellent agreement with experiment.

In our previous studies on aniline²¹ and phenol⁵⁷ we have demonstrated that the MP2 method is deficient in predicting the frequencies of some “troublesome” ring vibrations of aromatic molecules, whereas the B3LYP method overcomes this problem. Similar MP2 pitfalls have been noted for ozone and other molecules that have strong nondynamical correlation effects. Grimme⁵⁹ has shown for molecules with a complicated electronic structure that the nondynamical (long-ranged) correlations effects are usually overestimated by the MP2 method.

Thus, the discrepancies between the MP2 and B3LYP results concerning the structure of the C–NH₂ group and the predicted vibrational frequencies can be attributed to an overestimation of the nondynamical correlation effects in the standard MP2 calculations. The results obtained for adenine in this work as well as the previously reported studies for aniline²¹ and phenol⁵⁷ clearly demonstrate that the MP2-predicted frequencies may not be reliable, in some cases.

3.4. MP2 and CCSD(T) Complete Basis Set (CBS) Limit of Planarization Barrier. The barrier of planarization was calculated as the difference between the energy of the planar (constraint) and nonplanar (fully optimized) structures. Table 5 collects the planarization energies for adenine, obtained at different levels of theory. For comparison, we have also included the values reported by Wang and Schaefer,²⁰ who obtained the MP2-basis set limit barrier by assuming the additivity of the effects of core correlation and augmentation of basis set. According to their results, the planarization barrier of adenine amounts to 0.020 kcal/mol (7 cm⁻¹).

As is seen in the fourth column of Table 5, we have obtained a very similar value, 0.015 kcal/mol (5 cm⁻¹), by using a two-point extrapolation method to the complete basis set limit (CBS), on passing from the aug-cc-pVTZ to aug-cc-pVQZ basis sets (aTZ → aQZ). The MP2-planarization energy extrapolated for the aDZ → aTZ basis sets amounts to 0.098 kcal/mol (34 cm⁻¹). The last column of Table 5 shows the results obtained at the CCSD(T) level. The calculated value, 0.125 kcal/mol (44 cm⁻¹), is similar to that obtained at the MP2 CBS level with the same basis set extrapolation scheme (aDZ → aTZ). Thus, it is expected, that the use of the aTZ → aQZ basis sets, in extrapolation to the CCSD(T)/CBS limit, should yield planarization energy similar to that obtained at the MP2 level with the aTZ → aQZ extrapolation, but the computational time for the former method is prohibitively too large.

The other possibility for reaching the CCSD(T)/CBS level is to use the MP2/CBS value and to add the CCSD(T) correction term (Δ CCSD(T)). This term is defined as a difference between the MP2 and CCSD(T) relative energies, and it should be evaluated with a basis set that is as large as possible. Let us add here that the aDZ → aTZ extrapolation might be not

accurate enough due to a lower accuracy of the former term. Thus, summing the MP2/CBS value (5 cm⁻¹) and the Δ CCSD(T)/aTZ value (12 cm⁻¹) we obtain the CCSD(T)/CBS planarization barrier of 17 cm⁻¹, which clearly supports low values obtained from ref 20 and present MP2/CBS one. It should be noted that the calculated planarization barrier is much lower than the anharmonic zero-point-vibrational energy (ZPVE) of the NH₂ inversion mode (of about 90 cm⁻¹).

4. Conclusions

The amino group in adenine plays a key role in formation of hydrogen bonds in nucleic acids and in other molecular systems in living organisms. Thus, the problems of the nonplanarity of the C–NH₂ group and the planarization barrier in adenine are of the fundamental importance in the molecular recognition phenomena.

The results obtained in this study can be summarized as follows:

(1) The standard calculations at the MP2 level predict the nonplanar structure of adenine; however, larger basis sets tend to decrease the degree of pyramidalization of the C–NH₂ group. In contrast, the B3LYP method with different basis sets consistently yields the planar or nearly planar structure of adenine.

(2) The rotational constants calculated at various levels of theory cannot be used to conclude definitely whether the molecule is planar or not. Very good agreement with the experimental rotational constants has been obtained for both the planar structure calculated by the B3LYP method and the nonplanar structure obtained at the MP2 level. This indicates that pyramidalization of the C–NH₂ group has a very small influence on the calculated rotational constants.

(3) The planarization barrier of adenine has been calculated by the MP2 complete basis set (CBS) limit approach using the aug-cc-pVTZ → aug-cc-pVQZ (aTZ → aQZ) extrapolation scheme. The calculated energy barrier is negligible, 0.015 kcal/mol (5 cm⁻¹). This result is in very good agreement with the MP2-predicted barrier of 0.020 kcal/mol (7 cm⁻¹), reported earlier by Wang and Schaefer.²⁰

(4) Both the MP2/CBS and CCSD(T)/CBS calculations indicate that adenine, in the gas phase, has extremely flexible structure with a small energy barrier to planarization. This implies that the equilibrium structure of an isolated adenine shows only a small degree of nonplanarity, which does not support the conclusions made earlier that the NH₂ group in adenine is tilted about 20° out-of-plane.¹¹

(5) An extremely low planarization barrier implies that adenine requires very little energy to conform the structure of the amino group to formation of the complementary hydrogen bonds with other molecules. This fact is very important for base pairing in nucleic acids or other polymers containing adenine residues.

(6) The anharmonic frequencies of adenine calculated at the B3LYP/6–311++G(df, pd) level of theory are in excellent agreement with the available experimental data. Several reassignments of the bands in the IR matrix isolation spectra of adenine have been made. The predicted anharmonic frequency of the NH₂ inversion mode in adenine (N9–H tautomer) is 181 cm⁻¹, which is close to the experimental frequency, 184 cm⁻¹, determined from the neutron inelastic scattering (NIS) spectroscopy and supported by the N-deuteration data.

(7) Comparison of the theoretical IR spectrum calculated for the N9–H tautomer of adenine and the matrix isolation spectra indicates that some other tautomers of adenine may also be present in the Ar matrix.

(8) The MP2 method is deficient in calculations of the frequency of the NH₂ inversion mode in adenine. According to the potential energy distribution (PED) obtained in the MP2 calculations, there is no band assignable to NH₂ vibration, in the frequency region below 380 cm⁻¹. These results are contradictory to the experimental data. It is remarkable that the B3LYP method with the 6-311++G(df,pd) basis set predicts the IR spectrum of adenine in excellent agreement with experiment.

(9) The discrepancies between the MP2 and B3LYP results concerning the structure and vibrations of the C-NH₂ group in adenine can be attributed to an overestimation of the non-dynamical (long-ranged) correlation effects in the standard MP2 calculations.

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Supporting Information Available: Three tables containing harmonic vibrational frequencies (ω , cm⁻¹); IR intensities (A , km/mol); and PED for adenine calculated at the MP2/6-311++G(df,pd), MP2/6-31G(d), and MP2/cc-pVTZ levels of theory are available as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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