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A Theoretical Study of the Electronic Spectra of N_9 and N_7 Purine Tautomers

Antonio Carlos Borin

Universidade de São Paulo, Instituto de Química, C. P. 26077, 05599-970 São Paulo S. P., Brazil

Luis Serrano-Andrés

Departamento de Química Física, Universitat de València, Dr. Moliner 50, Burjassot,
E-46100 Valencia, Spain

Markus P. Fülscher* and Björn O. Roos

Department of Theoretical Chemistry, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden

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The complete active space (CAS) SCF method and multiconfigurational second-order perturbation theory (CASPT2) have been used to study electronic spectra of the N(9)H and N(7)H tautomers of purine. The calculations include vertical excitation energies, oscillator strengths, dipole moments, and transition moment directions in gas phase. In accord with experiment in nonpolar solvents, the two lowest $\pi \rightarrow \pi^*$ excited singlet valence states are predicted to be located at 4.7 and 5.1 eV. The latter is expected to shift to the red in aqueous solutions. A satisfactory interpretation of the electronic spectra above 5.5 eV is obtained if the experimental data are assumed to consist of the superposition of the spectra of the N(9)H and N(7)H tautomers. Two bands reported at 6.2 and 6.6 eV in nonpolar solvents match the corresponding ^1B_b and ^1B_a states of the N(9)H purine, respectively. The absence of the 6.2 eV-band in water can be explained by the predominance in aqueous solution of the N(7)H form, which has a weak ^1B_b transition at 6.4 eV overlapped by a strong ^1B_a transition at 6.6 eV.

1. Introduction

Detailed knowledge of the electronic structure of nucleic acids and related model compounds is important to understand the static and dynamic properties of polynucleotides. Reliable data, such as excitation energies, oscillator strengths, and transition moments in a molecule fixed frame are needed but difficult to extract from experimental data. For these reasons, we have computed these quantities, using ab initio quantum chemical methods, in systems of relevance in biochemistry, such as the nucleic acid monomers, cytosine,[1] thymine and uracil,[2] adenine and guanine,[3] protein chromophores, and related systems such as benzene,[4] pyrimidine,[5] naphthalene,[6] indole,[7] and imidazole.[8] In this paper we report calculations on the gas-phase spectrum of purine, describing vertical excitation energies, oscillator strengths, and transition moment directions for the most important electronic transitions to bear new insight into the controversial interpretation of the electronic spectrum of the nucleic acid monomers and to close the gap between simpler two ring systems and the nucleic acids.[19] The results are also compared to the spectroscopic properties of naphthalene, indole, adenine, and guanine.

Like adenine, purine exhibits prototropic tautomerism. The N(7)H tautomer is dominant in the solid state.[10] In aqueous solution purine exists as an approximately equal mixture of the N(7)H and N(9)H forms.[11−13] Recent experimental resonance Raman studies suggest that the N(7)H form is predominant[14] in water while theory seems to indicate a small predominance of the N(9)H form (52%).[15] In DMSO the N(9)H form is preferred (70%)[11,13] and in gas phase the N(9)H tautomer[15−19] is dominant.

Microwave,[16] IR,[17,18] UV,[20−22] and UV photoelectron[23] spectroscopy has been applied to characterize purine. The UV spectra obtained in matrix[22] and different solvents (methylcyclohexane (MCH),[20,24] trimethylphosphate (TMP),[20] and water[21]) can be described generically as being composed by four or five absorption bands (4.6−6.6 eV) attributed mainly to $\pi \rightarrow \pi^*$ transitions and a weak $n \rightarrow \pi^*$ band (4.0−4.3 eV). Further details of the band structure may be obtained from polarized reflection spectra of purine crystals[25] and linear (LD) and magnetic circular dichroism (MCD) spectra of substituted purine systems.[22,26,27]

In the present paper we have performed calculations on the electronic excited states of both tautomers in order to explain their optical properties. To describe the ground and electronic excited states of purine we applied the complete active space (CAS)SCF method supplemented by multiconfigurational, second-order perturbation theory, the so-called CASPT2 method. This approach has proven to be especially suited to investigate excited states of a broad spectrum of organic and inorganic molecular systems.[28,29] To the best of our knowledge, the present study is the first application of ab initio methods to investigate the electronic spectra of purine.

2. Methods and Computational Details

To perform the present calculations we followed as closely as possible the outline reported earlier for adenine.[3] Thus, we shall include only a brief summary.

The geometries of the N(9)H and N(7)H tautomers of purine were optimized assuming C_s symmetry and using the second-order Møller−Plesset (MP2) method in combination with

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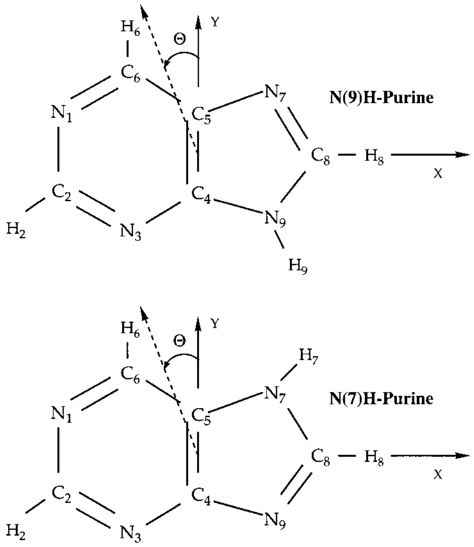

Figure 1. Molecular structures and atom numbering for N(9)H and N(7)H purine tautomers. The angle Θ gives the orientation (positive values) of transition dipole moment vector relative to the *y* axis, according to DeVoe−Tinoco convention. [flush left]

analytic derivative methods and 6-31G* basis set. Vertical excitation energies were then computed by the CASSCF/LS-CASPT2 method[28−30] (a level-shift value of 0.3 was applied) using atomic natural orbital (ANO) type basis sets[31] contracted to 4s3p1d functions for carbon and nitrogen, and 2s functions for hydrogen, respectively. In addition, the basis set was supplemented with an optimized set of 1s1p1d Rydberg-type functions placed in the molecular charge centroid and computed as explained elsewhere.[28]

To obtain the CASSCF reference functions we first performed an average calculation of 11 roots, including all 10 π -electrons, and 12 orbitals of a″ symmetry (nine valence π plus three Rydberg orbitals) in the active space. As we were interested only in valence states, the three Rydberg orbitals of a″ symmetry were deleted from the MO basis in subsequent calculations.[3] Finally, to compute the CASSCF functions of the lowest states of $^1A''$ symmetry we included the three orbitals of a′ symmetry and highest in energy (corresponding to the lone-pair orbitals on the nitrogens) in the active space in addition to the nine a″ valence π orbitals. All excitation energies were obtained using the ground state energy computed with the same active space employed for the calculation of the corresponding excited states.

The transition dipole moments were computed using the CAS state interaction (CASSI) method.[32] These were then used in combination with state energy differences calculated at the CASPT2 level to obtain oscillator strengths.

The geometry optimizations described in this section have been carried out using the Mulliken™ Version 2.25b[33] suit of programs. All other calculations have been performed with the MOLCAS-3[34] program package.

3. Results and Discussion

3.1. Ground State Properties. The structures, labeling, and definitions on the transition moment directions for the N(9)H and N(7)H tautomers of purine are shown in Figure 1. In this paper the ground state geometries were optimized at the MP2 level of calculation using 6-31G* basis sets.[33] The results are in agreement within 0.4 pm and 0.4° for bond distances and bond angles, respectively, with results from an earlier theoretical study[15] where the same method and the basis 6-311++G(2d,p) was employed. Larger discrepancies are found between the theoretical studies and the crystallographyic measurements,[10] which are attributed to N(7)H purine tautomer. Bond angles are reproduced with an accuracy of 1° or better. The predicted bond distances differ at most 1 pm from experiment apart from a few exceptions. The calculated $N_7{-}C_8$ bond distance of the N(7)H tautomer is predicted to be 4.5 pm longer as viewed by experiment. In addition, the C−H and N−H bond distances are also computed ≈0.1 Å longer than the measured values. In general, however, the position of hydrogen atoms can not be identified in the electron density maps obtained by X-ray crystallographic methods, and the calculated values are possibly more reliable.

The computed dipole moments (MP2/6-31G*) of the N(9)H and N(7)H tautomers of purine are 3.8 and 5.8 D, respectively. These values are reduced by 0.2 D at the CASSCF level using the ANO basis sets as described in section 2. The predicted dipole moments are in agreement with earlier theoretical investigations[15,17,18,35] and may be compared to the experimental value reported by Aaron et al.[36] 2.92 D, obtained in ethyl acetate. We also note that the large difference in dipole moments is in accord with the predominance of the N(9)H form of purine in the gas phase and apolar solvents. Furthermore, and in agreement with earlier studies,[15] the N(9)H molecule was computed to be more stable at the different levels of theory: MP2/6-31G* (16.7 kJ/mol), CASSCF/ANO (16.7 kJ/mol), and CASPT2/ANO (16.9 kJ/mol).

3.2. Singlet Excited Valence States of Purine. The UV spectra of purine in matrix,[22] crystals,[25] and dissolved in MCH,[20,24] TMP,[20] and water[21] are composed by a series of broad overlapping bands located between 4.6 and 6.6 eV. Therefore, we limited our calculations to singlet excited valence states with excitation energies lower than 7.0 eV. The results are presented in Table 1. The definition of the angles for the transition dipole moments directions appears on Figure 1 and follows the DeVoe−Tinoco convention.[37] The valence character of all studied excited states can be confirmed by comparing their computed CASSCF spatial extensions ($\langle r^2\rangle$, see Table 1) with that for the ground state. As can be noticed, they are very close to the ground state value, indicating the valence nature of the excited states.

For the N(7)H tautomer we predict the 2 $^1A'$ lowest excited singlet $\pi \rightarrow \pi^*$ state at 4.68 eV with an oscillator strength of 0.067. The wave function is dominated by a single configuration corresponding to the H → L (43%) (reference weight in parentheses) excitation, and the dipole moment, 4.61 D, is lower than that of the ground state, which indicates that its position may be blue-shifted in polar solvents. The letters H and L denote the HOMO and LUMO orbitals, respectively.

The 3 $^1A'$ state, located at 5.17 eV with an oscillator strength of 0.099, can be described by the electronic configuration originating from the H−1 → L (48%) excitation. In contrast to the 2 $^1A'$ state, the dipole moment of the 3 $^1A'$ state, 8.32 D, is much larger than that for the ground state. Thus, this state may be to shift to the red in polar solvents.

The 4 $^1A'$ state is located at 6.43 eV and dominated by the H → L+1 (35%) and H−2 → L (12%) excited configurations. It is characterized by a weak oscillator strength, 0.080, and a large dipole moment, 7.20 D. The 5 $^1A'$ state is predicted at 6.58 eV. The largest contribution to the wave function stems from the H−1 → L+1 (27%) excited configuration state function. The 5 $^1A'$ state carries most of the intensity—the calculated oscillator strength is 0.464—and the polarization angle is −40°. In contrast to all valence excited singlet states

TABLE 1: CASSCF (CAS) and CASPT2 (PT2) Vertical Excitation Energies (eV),[a] Dipole Moments (μ, D), and Spatial Extensions ($\langle r^2\rangle$, au) for the Singlet Excited States of Purine N(7)H and N(9)H Tautomers[b]

	purine N(7)H						purine N(9)H					
	excitation energies						excitation energies					
state	CAS	PT2	μ	$\langle r^2\rangle$	f	Θ	CAS	PT2	μ	$\langle r^2\rangle$	f	Θ
						$\pi \rightarrow \pi^*$ Transitions						
$1\,^1A'$			5.58	113					3.54	114		
$2\,^1A'$	5.08	4.68	4.61	116	0.0668	61	5.07	4.66	3.34	115	0.0340	−88
$3\,^1A'$	6.56	5.17	8.32	115	0.0985	−49	6.57	5.09	7.70	114	0.0632	−47
$4\,^1A'$	7.89	6.43	7.20	116	0.0797	4	7.75	6.28	5.32	116	0.1993	−11
$5\,^1A'$	8.24	6.58	5.89	117	0.4638	−40	7.29	6.36	2.19	117	0.0142	57
$6\,^1A'$	7.68	6.68	4.31	118	0.0328	−75	8.42	6.38	6.16	116	0.5657	−27
$7\,^1A'$	8.79	6.80	6.17	115	0.3091	−2	8.21	6.72	3.59	115	0.0187	−70
$8\,^1A'$	8.34	7.05	4.32	117	0.1300	60	8.89	6.81	3.73	116	0.2551	44
						$n \rightarrow \pi^*$ Transitions						
$1\,^1A''$	4.67	2.87	3.87	111	0.0060		5.17	3.76	2.87	111	0.0058	
$2\,^1A''$	5.77	3.90	3.87	111	0.0005		5.99	4.72	1.89	111	0.0036	
$3\,^1A''$	6.34	3.91	4.04	112	0.0029		6.61	4.85	2.41	112	0.0007	
$4\,^1A''$	6.79	4.53	3.86	112	0.0068		7.12	5.66	2.77	113	0.0141	
$5\,^1A''$	7.46	5.16	4.22	111	0.0017		7.87	5.87	4.61	112	0.0056	
$6\,^1A''$	7.87	5.27	4.00	112	0.0008		8.57	6.21	2.61	113	0.0002	

[a] Angles defined in Figure 1. [b] Oscillator strengths (f) and transition moment directions (Θ, degrees)[a] for the excitations from the ground to the indicated states are also included.

considered here, its dipole moment is close to that of the ground state and the band is expected to show only small solvatochromic effects.

It has been customary to name the lowest singlet excited valence states $2\,^1A'$ and $3\,^1A'$ according Platt's nomenclature as the ^1L_b and ^1L_a states, respectively. However, this match is not perfect as we are missing an important contribution from the H−1 → L excited configuration to the $3\,^1A'$ state. Likewise, we may assign the $4\,^1A'$ and $5\,^1A'$ states to Platt's ^1B_b and ^1B_a states, respectively. Here too, the correspondence with the ^1L_b and ^1L_a states may not be obvious on a first glimpse since the H−1 → L excited configuration hardly contributes to the wave function of the ^1B_b state. Table 2 compiles the structure (weights of the dominant configuration state functions) of the CASSCF wave functions for the computed states of the two purine tautomers.

Our calculations predict three additional singlet excited valence states with energies higher than 6.6 eV. The weakest calculated $\pi \rightarrow \pi^*$ transition is due to excitation from the ground to the $6\,^1A'$ state. The transition is located at 6.68 eV with an oscillator strength 0.033 and a low dipole moment, 4.31 D. The most important contribution to its wave function comes from the excitation H → L+2 (31%). The second strongest transition ($f = 0.31$) of the $\pi \rightarrow \pi^*$ spectrum is located at 6.80 eV and is associated to the $7\,^1A'$ state, for which the wave function is described by the following excitations: H−1 → L+1 (16%), H−2 → L (15%), H → L+1 (10%), H → L (9%), and H → L+2 (8%). The third strongest line is located at 7.05 eV ($f = 0.13$), and involves the $8\,^1A'$ state, described by a wave function composed mainly by the configurations originating from the H → L+1 (17%) and H−3 → L (20%) excitations.

The spectrum of N(9)H tautomer differs with respect to the spectrum of the N(7)H tautomer. The lowest $\pi \rightarrow \pi^*$ transition involves the $2\,^1A'$ state ($f = 0.034$, 4.66 eV), which can be described by three configurations: H−1 → L (25%), H → L (20%), and H → L+1 (19%). The transition to the $3\,^1A'$ state, located at 5.09 eV with an oscillator strength of 0.063 includes contributions from the following major configuration state functions: H → L (33%) and H−1 → L (22%). The strong configurational mixing render an assignment using Platt's notation more difficult. The best match is obtained assuming reverse state ordering as compared to the N(7)H tautomer, that is, the lowest singlet $\pi \rightarrow \pi^*$ excitation corresponds to the ^1L_a state.

TABLE 2: Main Configurations and Weights (%) for the Lowest Valence $^1A'$ States of N(7)H and N(9)H Tautomers of Purine. CASSCF Wave Functions[a]

	purine N(7)H		purine N(9)H	
state	configuration	weight (%)	configuration	weight (%)
$1\,^1A'$	Hartree−Fock	87	Hartree−Fock	85
$2\,^1A'$	H → L	43	H−1 → L	25
	H−1 → L+1	14	H → L	20
	H−1 → L	10	H → L+1	19
$3\,^1A'$	H−1 → L	48	H → L	33
	H → L	9	H−1 → L	22
	H−2 → L	8	H−2 → L	9
	H → L+2	7		
$4\,^1A'$	H → L+1	35	H → L+1	30
	H−2 → L	12	H−2 → L	11
	H−1 → L+2	10	H−1 → L	7
			H−3 → L	6
$5\,^1A'$	H−1 → L+1	27	H → L+2	28
	H−2 → L	14	H → L	10
	H → L	9		7
	H−1 → L	6		6
$6\,^1A'$	H → L+2	31	H−1 → L+1	43
	H−2 → L +1	9	H−1 → L	9
	H−1 → L	6	H−1,H → L	7
	H−1 → L+1	6		
$7\,^1A'$	H−1 → L+1	16	H−2 → L +1	14
	H−2 → L	15	H−1 → L+2	13
	H → L+1	10	H−3 → L	12
	H → L	9	H−2 → L	6
	H → L+2	8		
$8\,^1A'$	H → L+1	17	H → L+1	18
	H−3 → L	20	H−2 → L	16
	H−1 → L+2	10	H−1 → L	13

[a]H: HOMO. L: LUMO.

In the energy range from 6.0 to 7.0 eV we computed three strong transitions located at 6.28 ($4\,^1A'$), 6.38 ($6\,^1A'$), and 6.81 eV ($8\,^1A'$). In addition, the absorption spectrum is also predicted to include in this energy range two weak $\pi \rightarrow \pi^*$ excited singlet valence states placed at 6.36 and 6.72 eV. The $4\,^1A'$ state can be assigned to the ^1B_b state and includes the following characteristic configuration state functions: H → L+1 (30%) and H−2 → L (11%). Transitions to the $6\,^1A'$ state give rise to

TABLE 3: Interpretation of the Purine Spectra Based on the Experimental and Presently Computed Theoretical Excitation Energies (ΔE, eV), Oscillator Strengths (f), Dipole Moments (μ, D) of the Excited States, and Transition Dipole Moments Directions (Θ°, see Figure 1) of the Corresponding Excitations

Theoretical

N(9)H purine[a]				N(7)H purine[a]			
ΔE	f	Θ	μ	ΔE	f	Θ	μ
4.66	0.034	−88	3.3	4.68	0.067	61	4.6
5.09	0.063	−47	7.7	5.17	0.099	−49	8.3
6.28	0.199	−11	5.3	6.43	0.080	4	7.2
6.38	0.566	−27	6.2	6.58	0.464	−40	5.9

Experimental

MCH[b]		TMP[b,c]		crystal[e]			matrix[f]			7-methylpurine[f]			9-methylpurine[f]		
ΔE	ϵ^{d}	ΔE	ϵ^{d}	ΔE	f	Θ	ΔE	ϵ^{d}	Θ	ΔE	ϵ^{d}	Θ	ΔE	ϵ^{d}	Θ
4.7	8.0	4.7	6.9	4.7	0.093	48	4.7	7.6	−59/59	4.6	6.9	55/−25	4.7	4.2	53/−73
5.2	4.0	5.2	3.0	5.0			5.1	1.7	−52/52	4.9	2.1	−62/−88	4.9	4.5	−63/43
							5.8[g]	2.6	−54/54	5.6[g]	1.2	−38/68	5.5[g]	1.0	−53/33
6.2	20.0	6.2	18.1	6.2	0.350	51	6.2	15.5	−59/59	6.0	15.6	−46/76	6.0	17.6	−50/40
6.6	25.0	6.6	21.1												

[a] N(9)H (ground state $\mu = 3.5$ D) and N(7)H purine ($\mu = 5.6$ D) predominant in nonpolar and polar media, respectively. See text. [b] MCH: methylcylohexane.[20,24] TMP: trimethylphosphate.[20] [c] First and fourth bands equally observed in water.[21] See text. [d] ϵ: molar extinction coefficient multiplied by 10^{-3}. [e] Polarized reflection spectrum of purine crystals (N(7)H purine).[25] [f] UV in matrix (N(9)H-Purine); methyl derivatives in stretched films.[22] [g] The presence 177408n page of this band is unclear. See text.

the most intense band. This state is described by the electronic configuration originating from the single excitation H−1 → L+1 (43%), and therefore it may be classified as the $^{1}B_a$ state. The polarization angle of the transition vector is −27°. We also note that the dipole moments is almost twice a large as that of the ground state indicating large solvatochromic shifts.

A number of $n \rightarrow \pi^*$ singlet excited valence states have been computed for both tautomers of purine. All of them are characterized by small intensities. The three lowest $n \rightarrow \pi^*$ transitions are predicted at 2.87, 3.90, and 3.91 eV for the N(7)H tautomer of purine. For the N(9)H tautomer all the computed $n \rightarrow \pi^*$ transition energies appear to be shifted by ≈1 eV to higher energies. We also note that the dipole moments of the $n \rightarrow \pi^*$ excited states in N(9)H purine present larger variations (from 1.9 to 4.6 D) than in the N(7)H form (from 3.9 to 4.2 D).

3.3. The Electronic Spectrum of Purine. Experimental information on the electronic spectrum of purine is quite meager. Table 3 lists the available experimental spectral data and summarizes our theoretical results of both tautomers.

The low energy region of the spectrum of purine dissolved in several solvents was carefully studied.[20,21,22,24,25,38,39] Three bands were identified. A weak shoulder in the low-energy tail of the first band at 4.0−4.3 eV can only be observed in matrix,[22] crystals,[25] and apolar solvents, such as methylcyclohexane[24,38,39] and disappears in water.[21] This shoulder has been assigned to an $n \rightarrow \pi^*$ transition. The interpretation is consistent with a blue shift of $n \rightarrow \pi^*$ transitions in polar solvents leading to a strong overlap with the much more intense $\pi \rightarrow \pi^*$ transition lowest in energy.

At energies below 5.5 eV, two $\pi \rightarrow \pi^*$ transitions were identified. Albinsson and Nordén[22] measured the UV linear dichroism spectra of purine and several methyl derivatives in a matrix. Two transitions at 4.7 and 5.1 eV, respectively, were clearly identified, the former having larger intensity. Both transitions do not change significantly upon methyl substitution. In methylcyclohexane (MCH)[24,39] the first band is peaking at 4.7 eV and a second, weaker feature is observed near 5.1−5.2 eV. The latter band is observed more clearly in a mixture of methylcyclohexane−isopropanol.[24,39] In a somewhat more polar solvent such as trimethylphosphate (TMP) the band at 4.7 eV[20] remains. In contrast, the 5.1−5.2 eV-band is shifted to lower energies and only observed as a shoulder in the high-energy tail of the 4.7 eV-band. The spectrum of purine dissolved in water presents one single band at 4.7 eV in this region of the spectrum. Finally, the spectrum of purine crystals[25] has also two bands at 4.7 and 5.0 eV.

Mason[38] observed a shoulder in the electronic spectrum of 9-methylpurine dissolved in cyclohexane starting at 3.8 eV which disappeared in aqueous solution. The position of this band matches the weak feature found in the low-energy tail of the first band of purine and its methyl derivatives (see above). Considering that the computed values correspond to the systems in isolation, the transition could be related both to the $2^{1}A''$ or $3^{1}A''$ states of the N(7)H tautomer and the $1^{1}A''$ state of the N(9)H tautomer. That also indicates that there is a much lower unobserved $n \rightarrow \pi^*$ transition on N(7)H-purine close to 2.9 eV. In apolar solvents, where the N(9)H form of purine predominates[14] and the observed weak feature may be attributed to the $1^{1}A''$ state of the N(9)H tautomer, computed here at 3.76 eV. In polar solvents, however, the N(7)H tautomer will predominate and therefore the transitions to $2^{1}A''$ or $3^{1}A''$ states will also predominate, increasing the energy to ≈ 3.9 eV; on the other hand, and as indicated by the dipole moment of the associated states, the band maxima will shift to the blue and it will desappear beneath the more intense $\pi \rightarrow \pi^*$ band.

The band maximum at 4.7 eV can be readily assigned to the excitation to the $2\ ^{1}A'$ states of both tautomers. Moreover, in both cases the dipole moment of the excited and ground states are similar indicating, in accord with experiment, that the corresponding transition is hardly sensitive to the polarity of the solvent.

The transition to the $3\ ^{1}A'$ state is computed in the N(9)H purine at 5.09 eV with an oscillator strength 0.063 and in N(7)H purine at 5.17 eV with an oscillator strength 0.099. In both tautomers the excited state has a dipole moment around 3 D larger than that of the ground state. It can be therefore expected that the transition originated by excitation to the $3\ ^{1}A'$ state appears at much higher energies in nonpolar solvents than in polar solvents. This interpretation agrees well with the observed experimental spectra. In the less polar solvents, cyclohexane,[38] methylcyclohexane,[20,24] and trimethylphosphate,[20] a clear band is present at 5.1−5.2 eV with lower intensity than the first one.

The same holds true in the UV linear dichroism spectrum of purine in a (polyvinyl alcohol) matrix,[22] with a clear transition at 5.1 eV. In aqueous solution[21,24] one single band peaks at 4.7 eV, which is an indication that the transition to the 3 ^{1}A′ state has suffered a batochromic shift due to the high polarity of the related state. The observed band at 5.1−5.2 eV can be compared to the computed values for both purine N(7)H- and N(9)H tautomers at 5.17 and 5.09 eV, respectively.

In contrast to the observed intensity distribution of the two lowest $\pi \rightarrow \pi^*$ transitions, our calculations predict the excitations to the 2 ^{1}A′ states to be weaker than the promotions to the 3 ^{1}A′ states for both tautomers. The spectra of purine in matrix,[22] dissolved in cyclohexane,[38] and methylcyclohexane[20,24] show, however, that the lowest band, related to the 2 ^{1}A′ state, is much more structured than the band related to the 3 ^{1}A′ state. Similar features have been observed for indole:[7] The lowest $\pi \rightarrow \pi^*$ excited singlet state gives rise to an intense band with sharp vibrational structure, while the second band is a much broader and apparently corresponds to a weaker state. Here too, the computed oscillator strength, which represent total areas of the band, is larger for the second state.

There are suggestions on the presence of an extremely weak and in-plane polarized band around 5.6 eV in water[21] and 5.8 eV in matrix,[22] the latter decreasing to 5.5 eV in 9-methylpurine. We do not find any evidence of a $\pi \rightarrow \pi^*$ transition near the 5.8-5.5 eV region. It might be suggested that the higher lying $\pi \rightarrow \pi^*$ states could be shifted downwards by the solvent effects or that it is the 4 ^{1}A′ $n \rightarrow \pi^*$ state of N(9)H purine, computed with an oscillator strength of 0.014. The experimental evidences are not strong enough and therefore the presence of such a weak transition cannot be confirmed.

The absorption spectra of purine in MCH and TMP[20] present an intense band (see Table 3) with two peaks at 6.2 and 6.6 eV. The latter is the most intense band of the observed spectra. In water a single band is found at 6.6 eV, only, and is displaced to lower energies (6.2 eV) in strong acetic media. Assuming that the N(7)H tautomer is the most abundant form in aqueous solutions we find a perfect match of the computed and observed maximum of the most intense band, 6.58 ($f = 0.464$) and 6.6 eV, respectively. Because the dipole moment of the 5 ^{1}A′ state is comparable in magnitude to that of the ground state, this state, in accord with experiment, is not expected to expose large solvatochromic shifts. However, it renders to be more difficult to assign the less intense band observed at 6.2 eV in MCH and TMP which disappears in aqueous solutions.[20,21] The 4 ^{1}A′ state of N(7)H purine, located at 6.43 eV, is characterized by a dipole moment considerably larger than the ground state and thus, in contrast to experiment, it is expected to shift to lower energies in polar solvents. In addition, the 6 ^{1}A′ state is predicted to shift to the blue in polar solvents which would give rise to additional structure of the intense band. For these reasons, we prefer a different interpretation of the electronic spectra of purine above 5.5 eV, as explained below.

Tautomerism of purine has been observed experimentally using NMR[11] and resonance Raman[14] techniques. It has been concluded that both tautomers are present in about equal amounts in aqueous solution, with a slight predominance of the N(7)H purine. In DMSO and less polar media the N(9)H purine tautomer seems to be more abundant. Therefore, we have to take into account that both tautomers can participate in the absorption spectra.

Assuming that the electronic spectrum of purine in aqueous solutions can be interpreted as the superposition of the individual spectra of the N(9)H and N(7)H tautomers, the maximum at 6.2 eV can be readily assigned to the 4 ^{1}A′ state of the N(9)H tautomer computed at 6.28 eV. The corresponding state of the N(7)H purine tautomer is characterized by a 2 times smaller oscillator strength and thus will contribute considerably less. The second band at 6.6 eV may be attributed to transitions to the 6 ^{1}A′ state of the N(9)H purine (6.38 eV) and the 5 ^{1}A′ state of the N(7)H purine (6.59 eV). As the polarity of the medium increases, the N(7)H purine tautomer is present in a larger amount; therefore, the intensity of the third and fourth bands tend to decrease and increase, respectively (see Table [REF:tab:spectra]). In a polar environment such as water the third band is not observed, possibly because its strong overlap with the more intense fourth band.

The interpretation given above is consistent with results from magnetic circular dichroism studies[26,27] of several purine derivatives: Two low-lying transitions are followed by three higher medium to intense bands. However, because no gas phase spectra are available, it is difficult to extend the present analysis of the bands. For instance, it would be possible that the band computed at 6.80 eV in N(7)H purine contributes to the strong band in polar solvents at 6.6 eV. The present interpretation of the purine spectrum is, however, not in full agreement with that suggested by Albinsson and Nordén[22] for purine and three of its methyl derivatives, in which three $\pi \rightarrow \pi^*$ transitions are placed below 6.0 eV. These authors reported semiempirical calculations[22] at the CNDO/S level which support the presence of an additional, weak band close to 5.8 eV. The corresponding analysis of the UV/VIS and LD spectra is, however, debatable since the weak band peaks close to the deep through in the UV/VIS spectrum, is at the limit of the experimental setup, and overlayed by the signal of the strong band peaking approximately at 6.2 eV. Moreover, the CNDO/S results are misleading because the calculation were performed using not optimized, model geometries. Therefore, the excitation energies were underestimated by approximately 0.3 eV as compared to a equivalent calculation using an optimized ground state geometry. Unfortunately, also INDO/S calculations reported by Broo and Holmén[40] do not bear any new insight since the computed and experimental excitation energies of the known bands differ by ±0.4 eV.

We have also computed the transition dipole moments directions for both purine isomers (see Figure 1 for angles definition). The polarization vectors of the excitations to the two low-lying states in N(7)H purine, ^{1}L$_a$ and ^{1}L$_b$, do not point along the axis of the molecules and are almost perpendicular. A similar situation was found for indole[7] but is different from that in N(7)H adenine. The ^{1}B$_b$ and ^{1}B$_a$ bands have a short axis and an intermediate polarization, respectively, both in N(7)H purine and N(7)H adenine.[41] On the other hand, the N(9)H purine tautomer has a low-lying transition to a $\pi \rightarrow \pi^*$ state with a long-axis polarization and a second excitation with an intermediate polarization, differing from the situation in N(9)H adenine.[41] The short axis and intermediate polarization of the ^{1}B$_b$ and ^{1}B$_a$ bands of N(9)H purine also differ from the intermediate polarization of the N(9)H adenine[41] bands and is more similar to the situation found in indole.[7]

The computed transition dipole moment directions (see Figure 1) can be compared to those determined experimentally. Albinsson and Nordén[22] reported polarization angles of −59/59° for the low-lying $\pi \rightarrow \pi^*$ transition in N(9)H purine and selected the positive angle on the basis of their CNDO/S calculations. The CASSCF/CASPT2 method predicts a polarization angle of −88° which is consistent with the alternative choice, −59°. For N(7)H tautomer, the computed polarization

TABLE 4: Summary of Theoretical Values for Excitation Energies (ΔE, eV) and Oscillator Strengths (f) for Naphthalene, Indole, Purine, Guanine, and Adenine Derivatives

	^1L_b		^1L_a		^1B_b		^1B_a		
compound	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ref
naphthalene	4.03	0.000	4.56	0.050	5.54	1.337	5.93	0.313	6
indole	4.43	0.050	4.73	0.081	5.84	0.458	6.44	0.257	7
purine 9H	4.66	0.034	5.09	0.063	6.28	0.199	6.38	0.566	this work
purine 7H	5.17	0.099	4.68	0.067	6.43	0.080	6.58	0.464	this work
guanine 9H	5.09	0.231	4.76	0.133	6.65	0.161	6.66	0.479	41
adenine 7H	4.97	0.187	4.61	0.050	6.02	0.363	6.49	0.581	41
adenine 9H	5.13	0.070	5.20	0.370	6.24	0.851	6.99	0.565	41

TABLE 5: Configurations and Weights of Excited Configurations (Weight > 5%) for the Most Representative Valence Singlet Excited States of Naphthalene (Naph), Indole (Indo), N(9)H purine (9Pur), N(7)H purine (7Pur), N(7)H adenine (7Ade), N(9)H adenine (9Ade), and Guanine (Guan)

state	CSF[a]	Naph (%)[b]	Indo (%)[b]	9Pur (%)[b]	7Pur (%)[b]	7Ade (%)[b]	9Ade (%)[b]	Guan (%)[b]
^1L_b			$2\ ^1A'$	$2\ ^1A'$	$3\ ^1A'$	$3\ ^1A'$	$2\ ^1A'$	$3\ ^1A'$
	H−1 → L	37	44	25	48	25	31	−
	H → L+1	34	22	19	−	−	41	69
	H → L	−	−	20	9	−	13	7
	H−1 → L+1	−	−	−	−	14	−	−
	H → L+2	−	−	−	7	10	−	−
	H−2 → L	−	−	−	8	−	−	−
^1L_a			$3\ ^1A'$	$3\ ^1A'$	$2\ ^1A'$	$2\ ^1A'$	$3\ ^1A'$	$2\ ^1A'$
	H → L	76	54	33	43	42	63	68
	H−1 → L+1	10	7	−	14	17	−	−
	H−1 → L	−	5	22	10	−	−	−
	H−2 → L	−	9	9	−	−	−	−
	H → L+1	−	−	−	−	6	14	7
^1B_b			$6\ ^1A'$	$4\ ^1A'$	$4\ ^1A'$	$4\ ^1A'$	$4\ ^1A'$	$5\ ^1A'$
	H−1 → L	41	11	7	−	30	46	51
	H → L+1	40	42	30	35	10	26	−
	H−2 → L+1	−	7	−	−	−	−	3
	H−1 → L+1	−	−	−	−	−	−	14
	H−2 → L	−	−	11	12	−	−	−
	H−1 → L+1	−	−	−	10	−	−	−
	H−3 → L	−	−	6	−	−	−	−
^1B_a								
	$12\ ^1A'$	$6\ ^1A'$	$5\ ^1A'$	$7\ ^1A'$	$6\ ^1A'$	$7\ ^1A'$		
	H−1 → L+1	70	30	43	27	16	60	30
	H → L	6	6	−	9	28	−	5
	H−3 → L	−	6	−	−	−	−	−
	H,H → L,L	−	6	−	−	−	−	−
	H,H → L, L+1	−	5	−	−	−	−	−
	H−2 → L	−	−	−	14	−	−	−
	H−1 → L	−	−	9	6	−	−	−
	H,H−1 → L	−	−	7	−	−	−	−

[a] Main CSF (configuration state functions). H: HOMO. L: LUMO. [b] Weight of the configuration.

of the 4.7 eV band, 61°, is in agreement with the reported crystal value of Θ, 48°.[25] There is also good agreement between the computed value for the polarization of the 5.1 eV band of N(9)H, −47°, and the reported value in matrix, −52°,[22] if the negative polarization is selected.

3.4. Comparison of the Spectra of Purine and Related Compounds. In the following we compare the spectroscopic properties of bicyclic molecules naphthalene, indole, adenine, and guanine, and purine. A closely discussion focusing on the nucleic acids was presented some time ago[9] based on experimental data and semiempirical calculations. The present discussion will focus on the relation among the systems in the light of present and earlier CASSCF/CASPT2 *ab initio* studies.[3,6,7] Except for naphthalene, these systems contain an aromatic six-membered ring fused to an aromatic five-membered ring. As these systems are not isoelectronic—even not within the π -space—the comparison will only focus on qualitative aspects. Excitation energies and oscillator strengths of the most characteristic states of naphthalene, indole, adenine, and guanine are collected in Table 4. Table 5 compiles the main characteristics of the wave functions of these compounds.

Naphthalene is the prototype system to which Platt's analysis and nomenclature[42] has been applied. The underlying model involves four orbitals: H−1, H, L, and L+1 and four electronic states. The ^1L_b and ^1B_b states are composed by the antisymmetric and symmetric combinations of the H → L+1 and H−1 → L excitations, respectively. The ^1L_b state corresponds to the 'minus state' with weak intensity and the ^1B_b state is represented by the symmetric combination giving rise to a strong intensity. The oscillator strength of the ^1L_b and ^1B_b will decrease/increase the larger the interaction between the H → L+1 and H−1 → L excited states is. In naphthalene both excitations interact strongly. This is reflected in the composition of the wave function in Table 5, which shows the mixed character of the wave function for both ^1L_b and ^1B_b states. To the contrary, the ^1L_b and ^1B_a states are plus states mainly described by one single configuration, H → L and H−1 → L+1, respectively.

As all molecules, except for naphthalene, included in the present comparison belong to the C_s point group, additional configurations are allowed to participate in the description of the states. By inspection of Tables 4 and 5 we observe, however, that the structure of the spectra of all systems is very similar:

Two weak to medium intense bands (^1L_b and ^1L_a) located near 4.4−5.1 and 4.6−5.2 eV are followed by two medium to intense bands (^1B_b and ^1B_a) separated from the two lowest transitions by a gap of at least 1 eV, and located approximately near 5.8−6.6 and 6.4−7.0 eV. Of these four states, the ^1B_b and ^1B_a are always the third and fourth states, respectively, while the order of the low-lying states can vary. Additional states can appear at intermediate positions.

Indole and N(9)H adenine can be immediately recognized as systems where the configurational mixing between the H → L+1 and H−1 → L excitations is larger for the ^1L_b and ^1B_b states, while the ^1L_a and ^1B_a states are basically described by one single excitation. This configuration mixing is also reflected in the relative intensities. In both molecules the ^1L_b state is the lowest one with a weak transition intensity while the excitation to the ^1B_b state is enhanced to lead to the strongest transition of the computed spectrum. On the other hand, the ^1L_a and ^1B_a states lead to transitions which are more intense than the transitions to the ^1L_b and less intense than to those of the ^1B_b states, respectively. The N(9)H purine represents an intermediate situation where the configurational mixing in the ^1L_b and ^1B_b state is not so pronounced. The ^1L_b is still the lowest one, but the transition to the ^1B_b state does not enhance its intensity as much as in the previous compounds. Therefore, the strongest transition of the spectrum goes to the ^1B_a state.

N(7)H adenine, N(7)H purine, and especially N(9)H guanine, present a different structure. Their wave functions describe the states as basically singly configurational states, in particular for guanine. The consequence is that the states can be considered all of them as plus states involving transitions with varying intensities. In these three molecules the ^1L_a-type state (although the nomenclature is becoming meaningless here) is the lowest one leading to transitions of less intensity while the ^1L_b and ^1B_b states are intermediate states. The ^1B_a state is now the highest of the four states and leads to the strongest band in the computed spectrum.

The present assignments nicely correlate with the observed experimental spectra (see refs 7 and 41). For indole and adenine spectra we find two weak L bands. The third band can be attributed to the ^1B_b state and is the strongest oscillator (note than N(9)H adenine predominates in solution). In purine and guanine spectra it is the fourth band which is the most intense one, that is, related to the ^1B_a state. In purine this is independent of which tautomer predominates, although it seems confirmed that the N(7)H purine is more abundant in polar media.

4. Summary and Conclusions

The CASSCF/CASPT2 method has been applied to compute a large number of excited singlet valence states of N(7)H-purine and N(9)H-purine (cf. Figure 1). We have found that a full understanding of the electronic spectra of purine in different solvents can only be achieved when the presence of both N(7)H and N(9)H tautomers is taken into account. This conclusion is similar to that obtained in our previous study of the electronic spectra of adenine and guanine.[41] The present results differ, however, from that study in that the effect of the prototropic tautormerism on the electronic spectrum of purine in polar solvents is predicted to be stronger than for adenine. In agreement with the most recent experimental[14] and theoretical[15] investigations, electronic absorption spectra of purine are satisfactorly explained when the N(9)H purine is considered predominant in gas phase and nonpolar solvents and the N(7)H purine (a more polar molecule) is assumed to slightly predominate in polar solvents like water.

In nonpolar solvents two bands have been observed at 4.7 and 5.1−5.2 eV (see Table 3). The second one has been showed to decrease in energy in polar solvents and therefore the aqueous spectrum of purine[21] has one single band peaking at 4.7 eV. The assignment of these two bands can be performed either for the N(9)H or the N(7)H purine tautomers, because their 2 $^1A'$ and 3 $^1A'$ state have the same characteristics. In N(9)H purine the transition to the 2 $^1A'$ state is computed at 4.66 eV with a relative intensity 0.034. In N(7)H purine the same transition is computed at 4.68 eV with a oscillator strength 0.067. In both cases the dipole moments of the states are similar to the ground state dipole moments and therefore the corresponding excitation energy will be insensitive to the solvent polarity. The situation is different for the band related to the 3 $^1A'$ states, computed at 5.09 and 5.17 eV in N(7)H and N(9)H purine, respectively. These states have both large dipole moments and therefore the excitation energy will strongly decrease in polar solvents like water; this fact would explain the spectrum of purine in aqueous solution. For the higher bands of the spectrum the combined presence of both tautomers in solution seems necessary to fully explain the observed features. Two bands reported at 6.2 and 6.6 eV in nonpolar solvents match the corresponding ^1B_b and ^1B_a states of the N(9)H purine. The absence of the 6.2 eV-band in water can be explained by the predominance of the N(7)H form in aqueous solution which leads to a weaker ^1B_b transition at 6.4 eV and a stronger ^1B_a transition at 6.6 eV which probably overlaps the former.

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