Electronic Structure and Spectra of Imidazole, Purine and some Aminopurines

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A semi-empirical self-consistent field method of the Pariser-Parr-Pople type has been applied to purine and aminopurines. Both electronic transitions and ground state properties have been calculated and are found to be in harmony with observations. Similar calculations for imidazole have also been carried out. A comparison is made between purine and its two parent compounds pyrimidine and imidazole. The significance of both these compounds for the properties of purine is stressed. The equilibrium between the two isomers, 9H-purine and 7H-purine, is discussed. The importance of both isomers for the various properties of purine is pointed out.

I. INTRODUCTION

In a series of recent papers,[1–5] methods for the determination of semi-empirical parameters in different π-electron systems (for hydrocarbons,[1,2] for nitrogen containing molecules,[3] for chlorine containing molecules,[4] and for oxygen containing molecules [5]) have been discussed. It is essentially a SCF—MO—LCAO—CI method in the Pariser-Parr-Pople (PPP) approximation, formally implying zero-differential overlap (ZDO) [6] and semi-empirical determination of some integrals.

In the present paper, the above-mentioned method has been applied to the 9H- and 7H-isomers of purine and some related compounds, *i.e.* imidazole, 2-aminopurine, 6-aminopurine (adenine), 8-aminopurine, 2,6-diaminopurine, and 2,6,8-triaminopurine. The investigation includes calculation of ground state properties (*e.g.* electron densities, bond orders, and bond lengths), ionization potentials, singlet transition energies, oscillator strengths, and the polarization direction of the transition moments. The calculated values are found statisfactory when compared with the available experimental data as well as with other reported calculations of a similar type.

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II. THE METHOD

The details of the background for the parameter choice have been discussed in the previous papers [1-6] and will not be presented here. The values of the different parameters used in the present calculation are given in Table 1. They are exactly the same as used previously for calculations of other nitrogen-containing molecules.[3]

Table 1. Semi-empirical parameters for heteroatomic molecules containing nitrogen.

Carbon [1,2] $R_{CC}°=1.397$ Å		Pyridine-nitrogen [3] $R_{CN}°=1.338$ Å	Pyrrole-nitrogen [3]
$\gamma_{\pi\pi}$	11.97 eV	$\gamma_{\pi\pi}$ 15.44 eV	15.44 eV
$\gamma_{CC}°$	6.91 eV	$\gamma_{CN}°$ 7.16 eV	6.34 eV
$\delta_{CC}{}^{\gamma}$	-3.99 eV/Å	$\delta_{CN}{}^{\gamma}$ -3.99 eV/Å	-3.99 eV/Å
$\beta_{CC}°$	-2.42 eV	$\beta_{CN}°$ -2.72 eV	-2.25 eV
$\delta_{CC}{}^{\beta}$	3.05 eV/Å	$\delta_{CN}{}^{\beta}$ 2.6 eV/Å	2.6 eV/Å
$W_C°$	-9.84 eV	$W_N°$ -12.57 eV	-8.52 eV
$\Delta W_C°$	0.07 eV	$\Delta W_N°(C)$ 0.14 eV	0.14 eV
$\delta_{CC}{}^{W}$	9.22 eV/Å	$\Delta W_C°(N)$ 0.03 eV	0.03 eV
		$\delta_{CN}{}^{W}$ 5.6 eV/Å	5.6 eV/Å

The ZDO assumptions and notations and equations used for the evaluation of the various integrals are as follows:

$$S_{\mu\nu} = (\mu|S|\nu) = \delta_{\mu\nu}$$

$$\alpha_\mu = (\mu|H^{core}|\mu) = W_\mu - (n_\mu - 1)\gamma_{\mu\mu} - \sum_{\mu\neq\nu} n_\nu\,\gamma_{\mu\nu}$$

$$\beta_{\nu\mu} = (\mu|H^{core}|\nu)\begin{cases} \neq 0, \text{ when } \mu \text{ and } \nu \text{ are neighbours} \\ = 0, \text{ when } \nu \text{ and } \mu \text{ are non-neighbours} \end{cases}$$

$$(\alpha\beta|1/r_{12}|\mu\nu) = \delta_{\alpha\mu}\,\delta_{\beta\nu}\,\gamma_{\mu\nu}$$

Here, n_ν is the number of electrons contributed to the delocalized π-electron system by the orbital ν. Furthermore,

$$W_\mu(P,Q\ldots) = W_\mu° + \sum_{\substack{P \text{ over} \\ \text{all bonded} \\ \text{atoms}}} [\Delta W_\mu°(P) + \delta_{\mu P}{}^W(R_{\mu P} - R_{\mu P}°)],$$

$$\beta_{\mu\nu} = \beta_{\mu\nu}° + \delta_{\mu\nu}{}^{\beta}(R_{\mu\nu} - R_{\mu\nu}°),$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}° + \delta_{\mu\nu}{}^{\gamma}(R_{\mu\nu} - R_{\mu\nu}°), \text{ between nearest neighbours.}$$

$R_{\mu P}$ and $R_{\mu\nu}$ are the distances between atoms and $R°$'s are suitably chosen standard lengths (CC = 1.397 Å, CN = 1.338 Å). The integrals $\gamma_{\mu\nu}$ for non-neighbours have been calculated by the ball approximation. $\gamma_{\mu\mu}$ is the value of the one-center two-electron integral.

The SCF—MO's have been evaluated by means of a data machine programme written by P. Eisenberger, T. Alm and B. Roos. This programme also calculates the energy levels of the excited states by mixing all configurations obtained from single excitations. Oscillator strengths for the dipole transitions and eigenvectors for the multi-configurational problem are also obtained directly from the computer. The CDC 3600 machine has been used for the present calculations.

A suitable geometry for the molecules was chosen to start with and bond order values $p_{\mu\nu}$ were obtained. These values were then used to calculate the bond lengths by the relations [7]

$$R_{\mu\nu}(CC) = 1.517 - 0.180 \; p_{\mu\nu}$$

$$R_{\mu\nu}(CN) = 1.458 - 0.180 \; p_{\mu\nu}$$

If the $R_{\mu\nu}$'s thus obtained, deviated by more than ± 0.01 Å from the input value for any bond, the calculation was repeated with the obtained values as input for the new geometry. This procedure was continued until self-consistency was achieved. (The final values of $R_{\mu\nu}$ never deviated from the previous cycle by more than ± 0.002 Å in any case).

The numbering of the atoms in the various molecules is given in Fig. 1. The figure also indicates the choice of coordinate axes. The direction of the transition moment was taken as positive in the anticlockwise direction with respect to the y axis in conformity with the choice of DeVoe and Tinoco.[8]
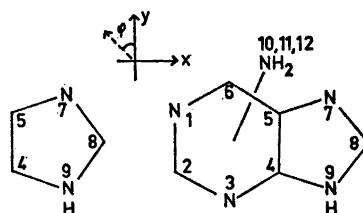

Fig. 1. Choice of coordinates and polarization angle ϕ as well as numbering of the atoms of imidazole and the purines.

III. RESULTS AND DISCUSSION

On account of the great biological importance of nitrogen bases a large amount of investigations, both experimental and theoretical, have been devoted to purine and purine derivatives. In connection with his recent theoretical work on purine and its amino derivatives Kwiatkowski has given very complete reviews [9,10] of both kinds of previous studies of these compounds. Therefore, such reviews will not be given here. Only the papers most pertinent in the present context will be mentioned.

A. Ground state properties

1. *π-Charges and bond orders.* The charges and the bond orders of 9H-purine * and of its two parent compounds, pyrimidine and imidazole, are

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* In the following, the word "purine" will always refer to the 9H-isomer.

Table 2. Calculated π-electron distributions in purine and in its parent compounds.

Position	Pyrimidine [3]	Imidazole	9H-Purine	Diff.
		π-Charges		
6	0.960		0.948	−0.012
1	1.069		1.097	+0.028
2	0.944		0.960	+0.016
3	1.069		1.138	+0.069
4	0.960	1.072	0.966	
5	0.998	1.094	1.016	
7		1.142	1.165	+0.023
8		1.037	1.015	−0.022
9		1.654	1.695	+0.041
		Bond orders		
5−6	0.661		0.560	−0.101
6−1	0.675		0.728	+0.053
1−2	0.660		0.603	−0.057
2−3	0.660		0.711	+0.051
3−4	0.675		0.585	−0.090
4−5	0.661	0.777	0.582	
5−7		0.558	0.465	−0.093
7−8		0.777	0.814	+0.037
8−9		0.479	0.453	−0.026
9−4		0.480	0.413	−0.067

compared in Table 2. It is seen that the order of the central bond, C_4—C_5, is lower in purine than in the separate rings. The rest of the bonds are less uniform than in pyrimidine and imidazole, the purine bond orders ranging from 0.4 to 0.8. Similar trends have been found in other cases of fused rings. For example, in naphthalene the bond lengths vary between 1.37 and 1.42 Å; *cf. e.g.* Ref. 1. It should be noted that the calculated electron densities of purine indicate a flow of electrons from the imidazole part towards the pyrimidine part.

Table 3 lists the electron distributions of the various 9H-purine derivatives and of 7H-purine. As is well known, the chemical shift of the proton magnetic resonance is related to the local π-electron charge of the carbon atom to which the hydrogen is bonded. However, several corrections must be applied to the measured relative shift before such a relationship can be established. These corrections have recently been analysed and estimated by Black and co-workers.[11] These authors have found that in several molecules both the relative order and the signs of the corrected shifts are different from those of the measured ones. Since the values of the various corrections are still debated, it seems to be most sensible to compare measured shifts and calculated π-charges q_i of a whole series of molecules rather than of a single molecule. It is, nevertheless, gratifying to note that the order of the π-charges of 9H-purine from our calculation, *i.e.* $q_8 > q_2$, q_6, is the same as that of Black *et al.*[11] It should also be observed that the net charges, obtained by our scheme, are

Table 3. Electron distributions in 9H-purine derivatives and in 7H-purine.

Atom or bond	π-Charge or bond order						
	9H-Purine	Adenine (6-Amino)	2-Amino	8-Amino	2,6-Diamino	2,6,8-Triamino	7H-Purine
1	1.10	1.17	1.15	1.10	1.23	1.23	1.08
2	0.96	0.96	0.92	0.97	0.91	0.92	0.98
3	1.14	1.17	1.21	1.14	1.24	1.24	1.07
4	0.97	0.97	0.96	0.98	0.96	0.98	1.00
5	1.02	1.07	1.04	1.01	1.09	1.09	0.98
6	0.95	0.90	0.94	0.95	0.90	0.91	1.02
7	1.16	1.18	1.16	1.25	1.18	1.25	1.70
8	1.01	1.03	1.03	0.96	1.04	0.99	1.01
9	1.69	1.69	1.70	1.73	1.70	1.73	1.16
10	—	1.87	—	—	1.87	1.88	—
11	—	—	1.88	—	1.88	1.88	—
12	—	—	—	1.89	—	1.90	—
1—2	0.60	0.61	0.56	0.62	0.56	0.57	0.60
2—3	0.71	0.71	0.67	0.70	0.67	0.66	0.72
3—4	0.59	0.57	0.58	0.60	0.57	0.57	0.57
4—5	0.58	0.60	0.59	0.58	0.60	0.61	0.59
5—6	0.56	0.51	0.55	0.57	0.51	0.52	0.57
1—6	0.73	0.68	0.74	0.71	0.69	0.68	0.73
5—7	0.46	0.47	0.46	0.45	0.47	0.45	0.41
7—8	0.81	0.81	0.82	0.77	0.81	0.78	0.45
8—9	0.45	0.45	0.44	0.43	0.44	0.42	0.82
4—9	0.41	0.42	0.41	0.38	0.42	0.39	0.45
6—10	—	0.37	—	—	0.37	0.36	—
2—11	—	—	0.36	—	0.36	0.35	—
8—12	—	—	—	0.33	—	0.31	—

of the same magnitude as those of the variable electronegativity method and thus considerably smaller than those of other SCF—MO methods.

The local charges on the pyridine-nitrogens can be related to their proton affinities. This problem has been studied by Nakajima and Pullman.[12] Here we find the same relative orders as previously obtained by Veillard and Pullman [13] and Berthod *et al.*,[14] *i.e.* in purine and adenine $q_7 > q_3 > q_1$ and in 2,6-diaminopurine $q_3 > q_1 > q_7$, which orders have been shown [13,14] to be in accord with experiments.

2. Dipole moments. The calculated π-parts of the dipole moments, μ_π, are shown in Table 4. A comparison with the measured total moments μ_{tot} of the last column is not straightforward. Moreover, recent attempts to calculate the σ-part of the dipole moment of sizable molecules [15] illuminate the difficulties inherent in such procedures. De Voe and Tinoco [8] calculated the σ-contribution by addition of bond moments and lone pair moments, and the π-part from Hückel MO calculations. In this manner they obtained theoretical moments in good accord with their experiments. It is interesting to note that their μ_π values of 9Me-purine and 9Me-adenine, *i.e.* 2.35 and 1.67 D, respectively, are rather close to our purine and adenine π-moments, 2.62 and 1.57 D.

Table 4. Calculated π parts of dipole moments μ_π of direction $\phi°$ (*cf.* Fig. 1). The increases $\Delta\mu_\pi$ refer to the constituents as discussed in the text. Observed total dipole moments are also listed. All moments in Debye.

Molecule		Calculation				Observation
	$-\phi°$		$\Delta\mu_{\pi x}$	$\Delta\mu_{\pi y}$	$\Delta\mu_\pi$	μ_{tot}
Aniline	1.60[3]		—	—		1.53 [16]
Pyrimidine	0.38[3]	60	—	—		2.44 [16]
Imidazole	2.87	162	—	—		—
9H-Purine	2.62	135	0.61	0.67	0.91	4.3 ± 0.2[a,8]
7H-Purine	3.16	38	0.70	−0.41	0.81	
6-Amino-purine	1.57	95	−0.28	+0.13	0.31	3.0 ± 0.2[a,8]
2-Amino- »	2.53	178	−0.35	+0.13	0.37	
2,6-Diamino »	0.90	188	−0.58	+0.16	0.60	
8-Amino »	4.16	199	+0.19	−0.14	0.24	
2,6,8-Triamino »	1.91	125	−0.50	−0.05	0.50	

[a] 9-butyl derivative.

Table 4 also shows the calculated increases $\Delta\mu_\pi$. In case of the purine isomers $\Delta\mu_\pi$ is the difference between μ_π of purine and the vectorial sum of the μ_π's of pyrimidine and imidazole. Both the purine isomers have positive values of $\Delta\mu_{\pi x}$, implying electron donation by the imidazole part to the pyrimidine part; *cf.* the above discussion of the π-charges. In case of the aminosubstituted purines $\Delta\mu_\pi$ is the difference between the μ_π of the considered compound and the vectorial sum of the μ_π's of purine and of aromatic amines,

Table 5. Calculated and experimental bond lengths in Å. Experimental standard deviations are given in brackets.

Bond	Imidazole		7H-Purine		Adenine	
	Calc.	Expt.[17] (0.005)	Calc.	Expt.[18] (0.010)	Calc.	Expt.[a,19] (0.010)
1—2	—	—	1.350	1.349	1.348	1.348
2—3	—	—	1.328	1.332	1.330	1.322
3—4	—	—	1.355	1.337	1.355	1.338
4—5	1.377	1.358	1.411	1.403	1.409	1.365
5—6	—	—	1.414	1.389	1.425	1.395
1—6	—	—	1.327	1.330	1.335	1.348
5—7	1.358	1.378	1.384	1.374	1.373	1.379
7—8	1.318	1.326	1.377	1.330	1.312	1.311
8—9	1.372	1.349	1.310	1.312	1.377	1.354
4—9	1.372	1.369	1.376	1.374	1.382	1.359
9—10					1.391	1.348

[a] 9-Methyl derivative.

μ_{π} of aniline being a typical value; cf. Ref. 3. It should be noticed that an amino group in the pyrimidine part gives rise to a larger (negative) value of $\Delta\mu_{\pi x}$ than the (positive) $\Delta\mu_{\pi x}$ value of the 8-amino compound. Thus, the amino substituents tend towards balancing the above-mentioned electron flow.

3. Bond lengths. In Table 5 calculated bond lengths are compared to molecular geometries obtained by X-ray analyses of crystal structures. The structure of 7H-purine has been determined by two entirely independent investigations,[18] one by Watson and the other by Sweet and Marsh. Except for systematic differences in the temperature factors, the two sets of results differ by less than their standard deviations. The values listed in Table 5 are the averages of the two sets. The reproduced standard deviation is that estimated by Watson (327 intensities observed). Sweet and Marsh have measured 570 intensities and estimated the standard deviation to be 0.006 Å. Both groups have found strong intermolecular hydrogen bonds between N_7 of one molecule and N_9 of the next in a chain of molecules with the hydrogen located on N_7.

The overall agreement between calculated and experimental bond lengths is seen to be satisfactory, particularly so in view of the possible discrepancies between molecular structures in vapour (calc.) and in crystals (expt.). In this context it is interesting to study the compilation of structures of purine and related compounds, published by Ringertz [20] in connection with a study of purine degradation. Among other things Ringertz has compared twelve different authors' structure determinations of adenine and its 9-substituted derivatives. As an example, the C_4-C_5 bond varies between 1.35 and 1.43 Å, the weighted mean being 1.374 ± 0.017 Å. The theoretical value is 1.409, outside the standard deviation of the mean but well inside the limits given by the various experiments.

Table 6. Ground state energies of the 9H- and 7H-isomers of purine. For comparison the corresponding values of benzene are also given. For definition of the various quantities, cf. the text and Ref. 21. All values in eV.

Energy term	9H-Purine	7H-Purine	Benzene
$E(\pi)$	-369.018	-368.616	-163.248
E(repuls.)	236.563	236.247	94.972
E(total)	-132.455	-132.369	-68.476
E(atoms)	-119.413	-119.413	-56.201
E(bonding)	-13.042	-12.955	-12.075

4. Ground state energies. In view of the experimental observation that the purine molecule most likely is the 9H-isomer and the 7H-isomer has been found in the crystal phase,[18] it is interesting to compare the stability of the two isomers. Table 6 reproduces various calculated energy terms. The definitions of these quantities have been given and discussed previously.[21] $E(\pi)$ is the energy of all the π-electrons moving in the core potential. E(repuls.)

is the interaction between the positively charged atomic cores. E(total) is the sum of these two terms and gives a measure of the stability of the molecule. Even more interesting is to calculate E(bonding) by subtracting the valence state energies of all the atoms, E(atoms), from E(total). It is seen from Table 6 that the effective bonding energy of the π-electrons of purine is very close to the corresponding value of benzene. Since there are ten π-electrons in purine and only six in benzene, the average bonding effect of each π-electron is obviously less in purine than in benzene in harmony with the chemical properties of the two compounds.

A comparison of the two purine isomers shows the 9H-purine to be more stable by an amount of 0.087 eV = 2.0 kcal/mole. This result is in conformity with observations of the free molecule. Moreover, Pullman et al.[22] have estimated the interaction between two purine molecules by various methods. They calculate a larger interaction energy in the 7H-dimer than in the 9H-dimer, the difference being around 4 kcal/(mole of dimer), which explains the transfer to the 7H-dimer in the solid state.

Table 7. Calculated and observed ionization potentials in eV.

Molecule	Calculation	Observation	
Aniline	7.66 [3]	7.71 ± 0.02,[23]	8.25 ± 0.02 [24]
Pyrimidine	9.50 [3]	9.47 ± 0.02,[23]	9.91 ± 0.05 [24]
Imidazole	8.35	—	
9H-Purine	8.15	9.68 ± 0.10 [25]	
7H-Purine	8.34		
6-Amino-purine	7.14	8.91 ± 0.10,[25]	7.8 [26]
2-Amino- »	7.09		
8-Amino- »	7.24		
2,6-Diamino »	6.60		
2,6,8-Triamino »	6.09		

B. I o n i z a t i o n   p o t e n t i a l s

The vertical ionization potentials (IP's), calculated by Koopmans' theorem, are given in Table 7. For comparison the values of aniline and pyrimidine are also reproduced. When comparing the calculated and the observed values it should be remembered that the present set of parameters have been adjusted to fit the adiabatic IP's, measured by Turner,[23] since no accurate vertical IP's are yet available. Values obtained by electron impact methods [24,25] are believed to be upper limits to the vertical IP's. The possible difference between adiabatic and vertical potentials is demonstrated by the two observed IP's of aniline and of pyrimidine reproduced in Table 7. The values calculated for the purines are seen to be rather low in comparison to experiments. However, the imidazole value seems to be very reasonable, being about 0.2 eV higher than the first IP of pyrrole.[23] Normally, IP values will decrease when the size of the molecule is increased. The calculated purine values are in

conformity with this trend. The experimental adenine IP of 7.8 eV, obtained from charge transfer spectra,[26] is probably less accurate than the other measurements.

C. Electronic spectra

The calculated values of singlet $\pi-\pi^*$ transition energies, the oscillator strengths and the directions of the transition moments are presented in Tables 8—10. Experimental values of transition energies and intensities obtained by different workers are also reported.

Table 8. Observed spectrum of pyrimidine in vapour and in various solvents compared to the calculated spectrum.

Calculation [3]		Observations					
		Vapour [36]		In methyl-cyclohexane [33]		In aq. soln.[32] pH 3.7	
ΔE	f	ΔE	f	ΔE	$\log \varepsilon$	ΔE	$\log \varepsilon$
5.22	0.01	5.27	0.05	5.12	3.30	5.10	3.51
6.70	0.30	6.72	0.16	6.53	3.78	6.60	3.72

Table 9. Electronic transition energies ΔE (in eV), oscillator strengths f, and polarizations φ (cf. Fig. 1), calculated for purine and its parent compounds pyrimidine and imidazole.

Pyrimidine [3]				Imidazole			Purine		
State	ΔE	f	$\phi°$	ΔE	f	$\phi°$	ΔE	f	$\phi°$
$B_2(B_{2u})$	5.22	0.01	30				4.88	0.05	102
				5.86	0.34	122	5.42	0.36	71
$A_1(B_{1u})$	6.70	0.30	120	6.47	0.04	64	6.31	0.47	147
							6.81	0.38	91
							7.08	0.47	78
$B_2(E_{1u})$	7.45	1.11	30	7.58	0.81	35	7.17	0.58	27
$A_1(E_{1u})$	7.64	0.86	120				7.73	0.19	119

A comprehensive study of the ultraviolet spectra of purine and its amino derivatives has been carried out by Mason [27] on buffered water solutions of the various compounds. In a recent series of papers Drobnik, Augenstein *et al.*[28-31] have reported absorption and emission properties of several of these compounds in different solvents. Many other investigations have been concerned with the spectra of purine and adenine. Voet *et al.*[32] have extended the observations in aqueous solution to 1850 Å. Clark and Tinoco [33] have

Table 10. Electronic transition energies ΔE (in eV), oscillator strengths f, and polarizations ϕ (*cf.* Fig. 1). Most of the observed values refer to buffered water solutions. Otherwise the solvent is indicated.

Calculation			Observations					
ΔE	f	$\phi°$	ΔE	$\log \varepsilon$	ΔE	f	ΔE	ΔE
9H-Purine								
			Refs. 27, 32		Ref. 33 [a,b]		Refs. 28—31[c]	
4.88	0.05	102	4.71	3.90	4.68	0.1	4.72	
5.42	0.36	71	5.3[s]		5.2[s]	0.05	5.1[s]	
6.31	0.47	147			6.2⎫			
6.81	0.38	91	6.6	4.37	6.6⎭	0.6		
7.08	0.47	78						
7.17	0.48	27						
7.73	0.19	119						
7H-Purine								
4.80	0.09	48						
5.63	0.13	124						
6.43	0.36	20						
6.46	0.86	94						
7.04	0.57	129						
7.41	0.18	84						
6-Aminopurine (Adenine)								
			Refs. 27, 32		Ref. 35		Ref. 33[a]	Ref. 34[d]
4.74	0.09	56	4.6[s]		4.61[s]	10^{-3}		
5.02	0.35	54	4.76	4.13	4.73	0.27	4.76	4.98
6.13	0.68	141	5.99	4.37	5.98	0.40	5.96	5.99
6.42	0.02	14						
6.67	0.29	147						
6.90	0.63	61			6.77	0.26	6.7	
7.26	0.06	107						
7.55	0.36	62			7.56[e]			
2-Aminopurine								
			Ref. 27				Ref. 29[g]	
4.55	0.16	76	4.06	3.78			4.05	
							5.0[i]	
5.15	0.44	94	5.25[s]	3.70			5.1[s]	
6.09	0.43	154					5.71	
6.45	0.21	137						
6.74	0.08	162						
6.85	0.48	75						
8-Aminopurine								
			Ref. 27					
4.74	0.16	80	4.38	4.16				
5.11	0.44	85	5.14	3.51				
6.09	0.40	145						
6.78	0.54	61						
6.86	0.22	0						
7.04	0.39	87						

Table 10. Continued.

2,6-Diaminopurine			Ref. 27		Ref. 33	Ref. 29 [h]
4.62	0.01	36	4.43	3.95	4.4	4.44
4.86	0.53	73			5.1	
5.91	0.85	147			5.8	
6.24	0.02	74			6.1	
6.54	0.22	6				
6.70	0.30	97				
2,6,8-Triaminopurine			Ref. 27			
4.54	0.05	36	4.23	4.08		
4.77	0.64	81	4.98	3.80		
5.89	0.68	148				
6.22	0.13	152				
6.60	0.28	36				
6.69	0.07	24				
6.76	0.30	114				

[a] In trimethyl phosphate. [b] f values evaluated by Berthod *et al.*[39] from spectra given in Ref. 33. [c] Various solvents. [d] Vapour phase. [e] Evaporated film method. [g] In dioxane. [h] In ethylene glycol-buffer. [i] Inflection. [s] Shoulder.

measured the spectra in less polar solvents and Clark *et al.*[34] the vapour spectra of adenine and related compounds. Tanaka and Nagakura [35] report absorption spectra of adenine both in aqueous solution and on quartz with an evaporated film technique. The latter is extended as far as to 1600 Å.

The present parameter set is fitted to reproduce vapour spectra. It is therefore instructive to consider solvent effects. Table 8 presents the pyrimidine spectrum in vapour phase and in two different solvents. It is seen that the solution spectra are red-shifted 0.1—0.2 eV compared to the vapour. The relative intensities are also changed.

Table 9 shows the calculated spectra of purine and of its parent compounds, pyrimidine and imidazole. As far as we are aware the only reports on the ultraviolet absorption of imidazole are the measurements by Leandri *et al.*[37] and by Gelus and Bonnier.[38] In both investigations ethanol was used as a solvent. A maximum was observed at 5.97 eV (log $\varepsilon = 3.70$) [37] and 6.00 eV (log $\varepsilon = 3.32$),[38] respectively. The calculated value of the first imidazole transition is seen to be in harmony with these observations. All the theoretical imidazole values are very similar to those calculated for pyrrole,[3] which values closely reproduce the vapour spectrum. Table 9 shows that the strong imidazole transition at 5.9 eV is intermediate in energy between the first two transitions (B_{2u} and B_{1u}) of pyrimidine. The second imidazole transition is weak. The third, very strong transition has almost the same energy as the E_{1u} transitions of pyrimidine. Accordingly, one must expect the higher purine transitions to carry features of both the pyrimidine and the imidazole spectra. In fact, a closer analysis of the transition densities indicates that the purine

bands are rather complex. The lowest transition at 4.9 eV is clearly related to the pyrimidine B_{2u} band. The next transition is, however, found to be a mixture of the B_{1u} band, the imidazole band, and an intramolecular charge transfer band. The higher transitions are even more complex.

In Table 10 the calculated and observed spectra of purine and the various amino derivatives are collected. Theoretical investigations of purine spectra including mixing of all singly excited configurations have been published previously. For a rather complete review of previous theoretical work, see Ref. 9. The spectra of purine and adenine have been studied by Berthod et al.[39] Very recently, Kwiatkowski [9,10,40,41] has investigated all the compounds collected in Table 10 with the exception of 7H-purine. These authors have used parameter sets, somewhat different from ours. Since there still are unclear points in the interpretation of the experimental findings it is interesting to compare the observations to the different theoretical results.

The spectrum of 7H-purine has been calculated recently by Song.[42] He does not state clearly whether mixing of several configurations has been included or not. His result that the spectra of the two purine isomers have different directions of polarization is nevertheless confirmed by the present calculations. Table 10 shows that the polarizations of the first two transitions are almost interchanged in 7H-purine compared to the 9H-isomer. In view of the small difference in bonding energies (Table 6) this result is very important for the interpretation of spectra obtained under different conditions. It seems as if the equilibrium between the two isomers may easily be shifted in the one direction or the other by change of solvent polarity, temperature, etc. In this context it is interesting to note the change of the broad absorption between 5 and 5.5 eV, when the solvent of purine is changed from trimethyl phosphate to methylcyclohexane and the temperature is raised to 80°C; cf. Fig. 2 of Ref. 33. The two maxima at 5.1 and 5.3 eV may be interpreted as due to the 9H- and 7H-isomers, respectively, corresponding to the calculated transitions at 5.4 and 5.6 eV; cf. Table 10. This interpretation is of course, only tentative. However, the possibility of a change in the isomer balance ought to be kept in mind.

Mason [27] observed that the ultraviolet spectra of substituted purines consist in general of two broad bands. In case of purine itself these lie around 4.7 eV and above 6 eV. Mason designated these bands as x and y bands, respectively. He also suggested that the x-band in purines is of composite nature, made up of two electronic transitions giving rise to x_1 and x_2 bands. These conclusions have recently been verified by Drobnik and Augenstein.[28] They found a clear separation of the x_1 and x_2 bands of purine when dissolved in methylcyclohexane, x_1 at 4.72 eV (262.7 mμ) and x_2 around 5.1 eV (242 mμ). According to them [30] the classification of Mason is found to be consistent for purine itself and for purines substituted at 2- or at 2,6-positions. But in the case of 6-substituted purines, the bands apparently lie so close together that they have not yet been resolved in absorption spectra, nor by polarization studies. However, Tanaka and Nagakura [35] have observed a shoulder at the long wavelength side of the first band of adenine. This shoulder can be interpreted as the x_1 band, the main absorption at 4.7 eV being the x_2 band. A similar interpertation can be given to the adenine absorption curve, published

by Voet et al.[32] Berthod et al.[14] have proposed and Kwiatkowski [10] has stressed such an assignment. The present results also support this interpretation.

In the present calculation the difference between the first two $\pi-\pi^*$ transitions are found to be: purine 0.54 eV, 2-aminopurine 0.60 eV, 2,6-diaminopurine 0.24 eV, and 6-aminopurine 0.28 eV. In accordance with experiments [27,33] these two bands are therefore expected to be more easily distinguishable in purine and 2-aminopurine than in other cases (cf. similar theoretical results by Berthod et al.[39]).

The bathochromic shifts of the first $\pi-\pi^*$ transition of the various mono-amino purines with respect to that of purine are as follows:

	Purine	>	6-amino	>	8-amino	>	2-amino
Exptl.[27-35]	4.71eV(263 mμ)		4.61(268)		4.38(283)		4.06(305)
Calc.	4.88(254)		4.74(261)		4.74(261)		4.55(272)

The same order is maintained although 6-aminopurine and 8-aminopurine are too close together. The calculated shifts in the first $\pi-\pi^*$ band obtained by introduction of more than one amino group are also in agreement with the order of observed data in the following cases:

	6-Amino	>	2,6-diamino	>	2,6,8-triamino
Exptl.[27-35]	4.61(268)		4.44(280)		4.23(293)
Calc.	4.74(261)		4.62(268)		4.54(273)

Also the observed hypsochromic shift from an amino group introduced in the 6-position of a 2-aminopurine is reproduced by the calculations

	2-Amino	<	2,6-diamino
Exptl.[27]	4.06(305)		4.44(280)
Calc.	4.55(272)		4.62(268)

Most observations have been made in the near ultraviolet above 200 mμ. However, for purine and adenine some measurements have been extended as far as to 160 mμ. The overall agreement between these measurements and the present calculations is quite satisfactory. For adenine Tanaka and Nagakura [35] have observed five absorption maxima. The first three at 4.61 eV $(f=10^{-3})$, 4.73 (0.27) and 5.98 (0.40) have their counterparts in the three lowest calculated transitions at 4.74 (0.09), 5.02 (0.35), and 6.13 (0.68). The following calculated transition, 6.42 eV $(f=0.02)$, may be difficult to observe. The next two theoretical transitions at 6.67 and 6.90 eV may be related to the observed maximum at 6.77 eV, and the calculated value at 7.55 eV to the observation at 7.56 eV.

Mason [27] has suggested that the first two transitions in purine and its derivatives are mutually perpendicular, the lowest one being longitudinally

polarized. Stewart and Davidson [43] have proposed that in 9-methyladenine crystals the first absorption band is polarized along the shorter axis (*i.e.* the C_4—C_5 bond) and is oriented at an angle of $3° \pm 3°$ from this axis towards the N_7 position.

Clark and Tinoco [33] have suggested that the lowest transition in adenine should be polarized at an angle of about $30°$ from C_4—C_5 axis towards the C_6 position and that the second band should be perpendicular to the first. They have also concluded that the polarization directions should be the same for 2,6-substituted purines. The observations by Drobnik *et al.*[31] is that the two lowest $\pi-\pi^*$ transitions are not parallel in purine and are oriented perpendicular to each other in 2,6-substituted purines. Stewart and Jensen [19] calculate two possible directions for the first band of 9-methyladenine crystals, *either* $-3°$, *cf.* Ref. 43, *or* $45°$, *cf.* Ref. 33.

The angles of the polarization directions of the different transitions are given in Table 10. The first transition in purine is found to be polarized along the longitudinal axis. The first transition in adenine is calculated to be inclined at an angle of $56°$ from C_4—C_5 axis towards the C_6 position, in accord with Ref. 33 and with one possibility of Ref. 19. The second band has a calculated polarization direction close to the first and the third transition is perpendicular to first, *cf.* Berthod *et al.*[39] The same is true for the first and third transitions in 2,6-diamino purine which appear to be roughly perpendicular to each other, *cf.* Kwiatkowski.[41]

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