Theoret. chim. Acta (Berl.) 10, 47—64 (1968)

Electronic Structure and Spectra of Organic Molecules

Part IV. The Pariser-Parr-Pople Type Calculations for Purine and Some of Its 6-Substituted Derivatives*

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Received November 6, 1967

The Pariser-Parr-Pople method has been used to calculate the π-electronic structures and spectra of 6-fluoro, 6-hydroxy, 6-methoxy, 6-amino, 6-methylamino, 6-dimethylaminopurine and their parent molecule purine. The purine and adenine (6-aminopurine) absorption spectra (singlet-singlet $\pi \rightarrow \pi^*$ type transitions) in particular are discussed in greater detail. The correlation among the absorption bands of the molecules in question and their ground state properties are also discussed. The theoretical results for singlet-singlet transition energies agree fairly well with the experimental data.

Mit der Methode von Pariser, Parr und Pople werden Struktur und Spektren der π-Elektronensysteme von Purin sowie 6-F-, 6-OH-, 6-OCH_3-, 6-NH_2-, 6-$NHCH_3$- und 6-$N(CH_3)_2$-Purin berechnet, wobei besonderes Gewicht auf spektrale Übergänge von Purin und Adenin gelegt wurde. Ferner wurde die Korrelation der Purin-Spektren mit den Eigenschaften des Grundzustandes untersucht. Die theoretischen Ergebnisse für Singulettübergänge stimmen ziemlich gut mit den experimentellen Daten überein.

A l'aide de la méthode Pariser-Parr-Pople nous avons calculé les structures et les spectres électroniques π d'une série de purines (purine, 6-F, 6-OH, 6-OCH_3, 6-NH_2, 6-$NHCH_3$ et 6-$N(CH_3)_2$-purine). L'accent a été mis en particulier sur les bandes d'absorption pour la purine et l'adénine. La corrélation entre les spectres d'absorption électronique et l'état fondamental de purines est étudiée. Les résultats théoriques concernant les énergies des transitions singulet-singulet sont en très bon accord avec les données expérimentales.

1. Introduction

Both experimental and theoretical studies on the properties of isolated nucleic acid bases seem to be of increasing importance from various points of view. For example, a knowledge of the optical properties of isolated nucleic acid bases (e.g. transition energies, polarization directions) allows to predict those for possible dimers and polymers of nucleotides. These predictions and the comparison of those with experimental measurements can be used to predict conformation and for structure determination of these polynucleotides.

The present paper is the first of a series devoted to the application of quantum mechanical calculations to the electronic structure and spectra of the purine and pyrimidine bases and related compounds. In the present paper the SCF MO CI calculations are presented for adenine and its parent molecule purine. Moreover the results of the same calculations for 6-fluoro, 6-hydroxy, 6- methoxy, 6-methylamino and 6-dimethylaminopurine are also included. Some aspects of the present study, viz. the relation between the absorption bands of purine and its 6-methoxy and 6-amino derivatives, have been recently discussed in a short note [1]. It

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* Submitted in honour of the seventieth birthday of Professor Aleksander Jabłoński.

should be pointed out that during the last three years systematic attempts, using the Pariser-Parr-Pople method [2], have been made to predict the electronic spectra and ground state properties of the nucleic acid bases (among them of adenine [1, 3—14]) and of some of their derivatives. As concerns the purine molecule itself, the electronic spectrum of this compound has been interpreted by means of the SCF MO method, with and without configuration interaction, by Berthod *et al.* [7, 8] and in our previous communications [1, 10, 13]. As far as we are aware, the electronic spectra of the other purines studied here have not been the subject of any theoretical studies by other investigators[1].

In Part V [15] the SCF MO CI method is applied to the study of the electronic spectra of some 2- and 8-substituted purines. Part VI [16] extends this consideration to some 9-substituted purines and adenines. The SCF MO CI calculations, similar to those presented here, are in progress for some 2,6-disubstituted purines. A recent paper [13] gives the results of the same calculations for adenine, 2,6-diaminopurine and 2,6,8-triaminopurine.

2. Method of Calculation and Choice of Parameters

The semiempirical SCF MO CI method is applied in the present paper to the study of the electronic structure of the molecules we are interested in. The details of the calculations are similar to those used in our previous papers dealing with the theoretical interpretation of the electronic spectra ($\pi \rightarrow \pi^*$ transitions) of monosubstituted benzenes, pyridines and pyrimidines [17—19].

The self-consistent field molecular orbitals were determined from the closed-shell SCF equations of Roothaan [20], in which the matrix elements of the Fock-Hamiltonian were written in the simple form used by Pople [21]. The evaluation of the core terms H_{pq}^{core} (the matrix elements of the one-electron Hamiltonian) and of the two-electron Coulomb repulsion integrals γ_{pq} is the same as that in our previous papers [17, 18]. One-center integrals γ_{pp} for the carbon and pyridine-type nitrogen atoms were obtained according to [22, 23] from the appropriate valence state ionization potentials, I, and electron affinities, A, i.e., $\gamma_{pp} = I_p - A_p$. For the one-center integral γ_{XX} (X indicates the atom contributing two π-electrons to the conjugated system) the value of 14.5 eV was used (see [17, 18]). All two-center two-electron Coulomb repulsion integrals γ_{pq} $(p \neq q)$ were evaluated from the formula due to Nishimoto and Mataga [24].

As regards the evaluation of the W_p integrals ($W_p = \langle \phi_p | T(i) + U_p(i) | \phi_p \rangle$), we proceeded as follows:

a) In the case when the p atom contributes only one π-electron to the system, we put the integral W_p equal to the negative value of the valence state ionization potential of atom p.

b) As to the evaluation of the W_p integral for the case when the atom p contributes two π-electrons, we adopted our previous approximation [25, 14, 17—19]. Namely, for the simple donor group X, in which there is only one atom contributing

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[1] It should be pointed out that Pullman [47] utilizing a very simple theoretical scheme (a perturbation treatment upon Hückel results) was the first to deal in a general way with the effect of substituents upon the 2630 Å absorption band of purine (cf. also [48]). We shall discuss some aspects of this publication in the forthcoming paper [15].

two π-electrons to the system, we put

$$\begin{aligned} W_X &= \langle \phi_X | T(i) + U_X^{++}(i) | \phi_X \rangle \\ &= \left\langle \phi_X \middle| T(i) + U_X^{+}(i) - \int \frac{|\phi_X(j)|^2 \, dv(j)}{r_{ij}} \middle| \phi_X \right\rangle \\ &= -I(\text{X–H}) - \gamma_{XX} . \end{aligned}$$

Here, I(X–H) is the first ionization potential of the X–H substituent and γ_{XX} is the two-electron one-center Coulomb repulsion integral.

The above approximation holds for such donor substituents as –F, –Cl, –Br, –J, –OR, –NR_1R_2 (the R's indicate the atom or group of atoms such as H, CH_3, C_2H_5 and so on). It is necessary to point out that the hyperconjugation effect of the R groups is indirectly taken into consideration by the use of the above approximation.

In the present calculations we tentatively adopted the value of -24.65 eV for the W_N integral for the pyrrolic nitrogen atom (see Table 1).

According to our previous suggestion [17, 18] the neutral penetration integrals occuring in the core integral are given by the "net" contribution of the neutral penetration terms. Namely, the neutral penetration integrals are essentially omitted, but the empirical correction δ_{C^*} ($= -0.6$ eV) is added to the value of the core integral of the carbon atom C* adjacent to a $-$X substituent or pyrrolic nitrogen atom [17].

The semiempirically evaluated values of one-electron core integrals W_p and two-electron one-center Coulomb repulsion integrals γ_{pp} are collected in Table 1.

The core resonance integrals β_{pq} were taken into consideration only for the nearest neighbours and their values were estimated in various manners (the

Table 1. *Semi-empirically evaluated values of W_p (in eV) and γ_{pp} (in eV)*

$2p$ atomic orbital		$-W_p$	γ_{pp}
Carbon[a] (tr tr tr π)		11.16[b]	11.13[c]
Nitrogen (pyridine-type, tr^2 tr tr π)		14.12[b]	12.34[c]
Nitrogen	in –NH_2 group	24.65 (10.15[d] + γ_{NN})	14.5[g]
	in –$NHCH_3$ group	23.70 (9.20[e] + γ_{NN})	
	in –$N(CH_3)_2$ group	23.30 (8.80[e] + γ_{NN})	
	pyrrole-type, –NH–	24.65[f]	
Oxygen	in –OH group	27.09 (12.59[d] + γ_{OO})	
	in –OCH_3 group	26.65 (12.15[e] + γ_{OO})	
Fluor		30.27 (15.77[d] + γ_{FF})	

[a] For the case of the carbon atom C* bonded with the atom contributing two π-electrons to the conjugated system the δ_{C^*} correction was added to the value of W_{C^*} ($\delta_{C^*} = -0.6$ eV, $W_{C^*} = -11.76$ eV).

[b] From Hinze and Jaffé [40].

[c] $\gamma_{pp} = I_p - A_p$. The values of the ionization potentials (I_p) and electron affinities (A_p) of appropriated valence states were taken from Hinze and Jaffé [40].

[d] Experimental values of the ionization potentials of the NH_3 (10.15 eV), H_2O (12.59 eV) and FH (15.77 eV) molecules [41].

[e] The values of I(X–H) chosen so as to reproduce a definite transition energy of monosubstituted benzenes (see [18]): N-methylaniline, $I(NH_2CH_3) = 9.2$ eV; N, N-dimethylaniline, $I[NH(CH_3)_2] = 8.8$ eV; anisole, $I(HOCH_3) = 12.15$ eV.

[f] The same value as in the case of the –NH_2 group.

[g] See [18].

exponential relation of Pariser and Parr [22], the R^{-6} relation of Kon [26] and the values of β_{pq} similar to those of Ladik and Appel [3]). The values of the resonance integrals (in eV) calculated by the use of these different approximations are listed in Table 2. It seems that this table is selfexplanatory.

Table 2. *Values of resonance integrals β_{pq} (in eV)*

$p-q$ bond[a]	For interatomic distances in adenine from the paper by Spences [27]			For interatomic distances in 9-methyladenine from the paper by Stewart and Jensen [28]		
	I–P[b]	II–L[c]	III–K[d]	IV–P[b]	V–L[e]	VI–K[d]
1, 2	−2.54	−2.39	−2.512	−2.30	The same as II–L	−2.318
2, 3	−2.54	−2.39	−2.512	−2.66		−2.605
3, 4	−2.54	−2.39	−2.512	−2.43		−2.424
4, 5	−2.67	−2.39	−2.579	−2.75		−2.636
4, 9	−2.14	−2.39	−2.198	−2.16		−2.207
5, 6	−2.53	−2.39	−2.469	−2.32		−2.314
5, 7	−2.03	−2.39	−2.103	−1.92		−2.022
6, 1	−2.54	−2.39	−2.512	−2.30		−2.318
7, 8	−2.27	−2.39	−2.297	−2.83		−2.739
8, 9	−2.54	−2.39	−2.512	−2.22		−2.257
6, 10	−2.40	−1.91	−2.402	−2.30		−2.318

[a] For the numbering of atoms see Figure.

[b] Estimated on the basis of the exponential relation of Pariser and Parr [22]: $\beta_{pq} = -A \exp(-5.6864\, R_{pq})$. The following values of the constants A (in eV) were used: A (for C–C bond $= 6465.23$ and A (for C–N or C–X bonds) $= 4895.71$.

[c] All resonance integrals for the ring assumed to be equal to $1.0\,\beta_0$ ($\beta_0 = -2.39$ eV). The resonance integrals for the external bond β_{6-10} assumed to be equal to $0.8\,\beta_0$. For comparison see [3, 42].

[d] Estimated on the basis of Kon's relation [26]: $\beta_{pq} = -A/R^6_{pq}$. The following values of the constants A (in eV · Å^6) were used: A (for C–C bond) $= 17.0519$ and A (for C–N or C–X bonds): 13.9060.

[e] For the explanation of this sort of calculations see text (Section 4).

Two different geometrical structures of the molecules in question were adopted in the present study. One of these is based on the most probable structure of adenine deduced by Spencer [27] and other one on the 9-methyladenine structure determined by Stewart and Jensen [28] by means of the x-ray crystal analysis technique. For all the external C_6–X_{10} bonds the value of 1.34 Å (the length of the C–NH_2 bond as proposed by Spencer [27]) and of 1.348 Å (the length of the C–NH_2 bond determined by Stewart and Jensen [28]) were used, respectively.

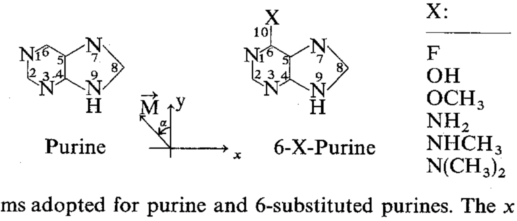

Fig.1. Numbering systems adopted for purine and 6-substituted purines. The x and y axes parallel to the molecular plane, the y axis passes through the C_4 and C_5 atoms. The transition moment (M) direction (the angle α) is defined. According to the suggestion of DeVoe and Tinoco [43] the transition moment directions are given positive towards C_6 with respect to an axis from C_4–C_5

The values of the N_1–C_6–X_{10} angles were the same as those for the N_1–C_6–N_{10} ones given in the above-mentioned structures of molecules. The numbering systems of the molecules under consideration are presented in Fig. 1.

As to the excited states, the configuration interaction was admitted and singly excited configurations were included. For the purine molecule all singly excited configurations, whereas for the 6-substituted purines fifteen singly excited configurations were allowed to interact. In the latter case the single excitations from the lowest occupied molecular orbital (m.o.) and the single excitations to the highest unoccupied m.o. were omitted. The oscillator strengths, f, for the transitions from the ground state to the excited states of the molecules were calculated from the Mulliken and Rieke formula [29].

3. Spectral Properties of Purine and Some 6-Substituted Purines

At this point it may be worthwile to review briefly some spectral properties of purine and its 6-substituted derivatives. We shall only be concerned with the singlet-singlet transition energies in these molecules. Some aspects of the lowest triplet states of purines will be discussed elsewhere.

3.1. Electronic Spectra, Oscillator Strengths

The near ultra-violet absorption spectra of purines and its 6-substituted derivatives (in particular of adenine) have been examined by several researchers. However, until Mason's paper [30], comparatively few works had been published on the absorption spectra of monosubstituted purines. Mason [30] was the first to measure the absorption spectra of a series of mono- and polysubstituted purines in aqueous solutions and to make an effort to classify their absorption bands. He observed that the spectra of these compounds consisted in general of two broad bands (called x and y), situated at 2600 and < 2200 Å in the case of purine. Because two bands lying close together have been observed in the spectra of 9-methylpurine in cyclohexane (at 2600—2400 Å) Mason proposed that the x band in purine and its 6-substituted derivatives is a composite one $(x_1 + x_2)$, a proposition confirmed more recently by Drobnik and Augenstein [32] (also see [31, 33, 37]). It should be added that Tanaka and Nagakura [9] extended the measurements of the adenine spectrum to the vacuum ultra-violet region (down to 1600 Å).

The relative positions of the lowest two $\pi \rightarrow \pi^*$ transitions in adenine and other 6-substituted purines seem to be of interest. Two $\pi \rightarrow \pi^*$ transitions are observed in 2650—2400 Å region in the purine spectrum: a strong absorption band x_1 (or S (= strong) band) with the molar extinction coefficient ε equal to ~ 7000 and a shoulder (the x_2 band or the W (= weak) band) at ~ 2400 Å with the ε value equal to about 3000. In the case of 6-substituted purines these two $\pi \rightarrow \pi^*$ bands lie close together in energy – one strong absorption band at 2600—2500 Å is observed in the ultra-violet spectra of these purines. However, the question of the relative position – in terms of energy – of these two lowest-lying $\pi \rightarrow \pi^*$ transitions still remains to be solved. Some investigators [9, 34, 35] observed a shoulder at 2670—2690 Å on the long-wave side of the 2600 Å band of the adenine spectrum and they postulated that this shoulder is a weak band covering one $\pi \rightarrow \pi^*$ transition. On the other hand, Clark and Tinoco [33] allocated this weak

Table 3. *Compilation of the spectral data (absorption) for purine and adenine*

Solvent	λ_{max}^{a}	ε^{b}	ΔE^{c}	f^{d}	References
Purine					
H_2O, pH = 5.70	2630	6.2	4.71	—	Mason [30]
	< 2200	12.0	> 5.6	—	
H_2O, pH = 5.8	2630	8.0	4.71	—	Voet *et al.* [44]
	1880	23.6	6.59	—	
TMP (trimethyl phosphate)	2650	6.9	4.68	0.1^{e}	Clark and Tinoco [33]
	2400 (sh)	3.0	5.17	0.05^{e}	
	2000	18.1	6.20	0.6^{e}	
	1880	21.1	6.59		
EPA	2610—2620	—	4.74	—	Cohen and Goodman [45]
Methylcyclohexane	2627^{g}	7.6	4.72	—	Drobnik and Augenstein [32]
	2420 (sh)	—	5.12	—	
Adenine					
H_2O, pH = 7.03	2600	10.0	4.76	—	Mason [30]
H_2O, at neutral pH	$2670^{h,i}$ (sh)	—	4.64	0.0^{i}	DeVoe and Tinoco [35]
	2590^{h}	—	4.79	0.30	
	2070^{h}	—	5.99	0.37	
H_2O, pH = 7.0	2605	13.4	4.76	—	Voet *et al.* [44]
	2070	23.2	5.99	—	
H_2O, at neutral pH	2600	—	4.76	0.28	Láng and Ladik [66]
	2070	—	5.99	0.54	
TMP (trimethyl phosphate)	2600	12.6	4.76	^{j}	Clark and Tinoco [33]
	2080	18.7	5.96	—	
	1850	15.8	6.70	—	
Vapour phase	2490^{k}	12.0	4.98	0.24	Clark *et al.* [46]
	2070	—	5.99	—	
EPA	2600	—	4.77	—	Cohen and Goodman [45]
H_2O, pH = 6.66	2690 (sh)	—	4.61	$\sim 10^{-3}$	Tanaka and Nagakura [9]
	2610	—	4.73	0.27	
	2070	—	5.98	0.40	
	1830	—	6.77	0.26	
Measured with the evaporated film method	1640	—	7.56	—	

[a] Data refer to absorption maxima: λ_{max} (in Å). The letters sh indicate a shoulder.

[b] The values given for ε must be multiplied by 10^3 in order to get molar extinction coefficients.

[c] Transition energy (in eV) corresponding to absorption maximum.

[d] Oscillator strength.

[e] Evaluated from the spectra given by Clark and Tinoco [33], see [8].

[g] The purine absorption maximum has been observed in several solvents (methylcyclohexane, dioxane, dichloroethane, isopropanol, methanol, H_2O) at ~ 2630 Å and in glycerol at 2640 Å.

[h] From the spectrum of deoxyadenosine.

[i] Postulated weak band seen as shoulder in adenine spectrum, see e.g. [34].

[j] For adenine the oscillator strength decreases from 0.28 in water to 0.24 in the case of the vapour phase [46].

[k] There is a misprint in Table I of the paper by Clark *et al.* [46]. The value of 2520 Å is given for the absorption maximum of adenine, while the value of 2490 Å is given for that of 9-methyladenine. From a comparison of the vapour phase spectra of adenine and 9-methyladenine given in Fig. 1 of the above paper it is obvious that these values for the absorption maxima should be interchanged (cf. also the text on page 3616 of the Ref. [46]).

band on the short-wave side of the strong absorption 2500—2600 Å band in 6-chloro, 6-methoxy and 6-aminopurine (cf. also [36, 37]). Kleinwächter *et al.* [38] postulated recently that the shoulder observed in some 6-substituted purines on the long-wave slope of the 2600 Å absorption band is vibrational in nature. Therefore they postulated that in adenine and other 6-substituted purines the weaker (*W*) band has a higher energy than the more intense (*S*) one.

Mason [30] studied the effects of substituents [among them of $-OH$, $-OCH_3$, $-NH_2$, $-NHCH_3$ and $-N(CH_3)_2$] upon the position of the *x* band (or *S* band) in the purine spectrum. The changes in the wave-lengths of maximum absorption of the *x* band induced by single substituents mentioned above, placed in the 6-position of the purine nucleus, as those observed by Mason [30], together with some other measurements, are given in Table 4. It is seen that some substituents are bathochromic and others hypsochromic. The order of increasing bathochromic shift may be expressed as $NHCH_3 < N(CH_3)_2$ and the order of increasing hypsochromic effect is $NH_2 < OCH_3 < OH$. It is noteworthy that the above-mentioned substituents, placed e.g. in benzene, exhibit the following order of increasing bathochromic shifst: $OH < OCH_3 < NH_2 < NHCH_3 < N(CH_3)_2$ (cf. our previous theoretical calculations for substituted benzenes, pyridines and pyrimidines [17—19]). An examination of the electronic spectra of the 2- and 8-substituted purines (e.g. [30]) shows that these substituents exhibit the bathochromic effect on the *x* band of the purine spectrum (cf. also forthcoming paper on the electronic spectra of 2- and 8-substituted purines [15]).

Table 4. *The shifts of the first (x) absorption band of purine upon substitution at the 6-position in purine nucleus*

Substituent	Shifts (in Å) measured relative to purine		
	Mason [30]	Voet *et al.* [44]	Clark and Tinoco [33]
$-OH$	−120		
$-OCH_3$	− 60		−140
$-NH_2$	− 30	−25	− 50
$-NHCH_3$	+ 30		
$-N(CH_3)_2$	+120		

Some attempt to explain the effect of the 6-OCH_3 and 6-NH_2 substituents on the spectrum of purine has been made in our previous note concerning the correlation among the absorption bands of purines [1]. Upon substitution of the OCH_3 or NH_2 groups at the 6-position of the purine nucleus the first two absorption bands, x_1 and x_2, of purine are shifted towards the longer wavelenghts. However, the second band (x_2) is displaced more than the x_1 band. Therefore, the bands observed at 2500 and 2600 Å in 6-OCH_3 and 6-NH_2-purine respectively are composed of two overlapping bands. Since the intensity of the first band is probably smaller than that of the other one, the near ultra-violet absorption bands observed in 6-substituted purines correlate with the x_2 band of purine.

3.2. The Direction of Polarization

As far as we are aware, the polarization direction of the electronic transitions in nucleic acid bases and their analogues have been determined only for 9-methyladenine, 1-methylthymine and their hydrogen-bonded complex [28, 36, 39]. The polarization direction of the first (main) absorption band of 9-methyladenine has been determined along the shorter axis, C_4–C_5. The measured transition moment direction is 3° ± 3° from the C_4–C_5 bond and inclined towards the N_7-position. The other weaker component (a shoulder) of the first long wavelength transition is suggested to be polarized at right angle to the first one. These researchers also suggest that the other absorption band ($\lambda_{\max} \approx < 2300$ Å) is also long-axis polarized.

Mason [30] on the basis of both comparisons the spectra of azaindenes and the effect of substituents upon the position of the x band in the purine spectrum suggested that the first ultra-violet absorption band has two $\pi \rightarrow \pi^*$ transitions oriented perpendicularly to each other with the lower energy transition having a longitudinal polarization. Clark and Tinoco [33], on the other hand, suggest that the 2600 Å band of adenine is polarized along the C_4–C_6 axis, i.e. about 30° from the C_4–C_5 axis and inclined towards the C_6-position.

4. Results of Calculations and Discussion

4.1. Spectroscopic Properties of Purines

The calculated singlet-singlet transition energies and oscillator strengths for the purine molecule together with some experimental data are given in Table 5. The results of the calculations as presented in this table were obtained by the use of various approximations on the core resonance integrals, β_{pq}, and of two different geometrical structures of the molecule. As shown in Table 5, the agreement of the spectrum calculated by means of different approaches with the observed values is in all cases satisfactory. It seems, however, that the results reported in the last two columns of Table 5 are more satisfactory than the others. The calculations mentioned above gave the f-values for the first two transitions, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, having practically the same values. If the purine geometry from Ref. [27] is used in the calculations, one obtains the value of the oscillator strength for the $S_0 \rightarrow S_2$ transition greater than for the $S_0 \rightarrow S_1$ one.

Table 5. *The comparison of calculated and observed singlet-singlet transition energies, ΔE (in eV), and oscillator strengths, f, for purine*

Transition	Calculated for interatomic distances from Ref. [27]						Calculated for interatomic distances from Ref. [28]				Experimental (see Table 3)	
	I–P		II–L		III–K		IV–P		VI–K			
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	
$S_0 \rightarrow S_1$	4.87	0.093	4.59	0.100	4.80	0.095	4.78	0.099	4.71	0.101	4.68	4.72
$S_0 \rightarrow S_2$	5.21	0.147	5.10	0.185	5.18	0.159	5.35	0.102	5.30	0.099	~5.17	~5.12
$S_0 \rightarrow S_3$	6.05	0.710	6.00	0.858	6.04	0.729	6.26	0.687	6.17	0.762	6.20	
$S_0 \rightarrow S_4$	6.55	0.296	6.54	0.379	6.54	0.338	6.57	0.528	6.55	0.497	6.59	
$S_0 \rightarrow S_5$	6.79	0.088	6.75	0.459	6.79	0.073	6.84	0.120	6.83	0.104		

A similar conclusion may be deduced from a comparison of the calculation results listed in Table 6 (for adenine), 7 (for aminoderivatives of adenine) and 9 (for 6-F, 6-OH and 6-OCH_3-purine). As seen from these tables, the calculations with the use of the Stewart and Jensen geometry for the molecule gave a value of the oscillator strength for the $S_0 \rightarrow S_1$ transition in 6-X-purines much smaller than for the $S_0 \rightarrow S_2$ one. Contrary to this, the calculations with the use of the Spencer geometry gave for both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions similar values of the oscillator strengths. As pointed out before (Section 3), from a comparison of the near ultra-violet absorption band of purine with its 6-substituted derivatives it may be concluded that the lowest-lying $\pi \rightarrow \pi^*$ transition in 6-OH, 6-OCH_3 and 6-NH_2-purine is the weak one. This assignment allows to explain the hypsochromic shifts (cf. Table 4) in the wave-length of the x band of purine upon substitution of the 6-OH, 6-OCH_3 and 6-NH_2 groups in the purine nucleus. Such a clear-cut conclusion concerning the relative location of the first two transitions does not hold in the case of the aminoderivatives of adenine, as both the 6-$NHCH_3$ and 6-$N(CH_3)_2$ substituents have the bathochromic effect on the x band of the purine spectrum.

Table 6. *The comparison of singlet-singlet transition energies, ΔE (in eV), and oscillator strengths, f, for adenine calculated by the use of different approximations for the resonance integrals, β_{pq}. For the experimental data see Table 3*

Transition	Calculated for interatomic distances from Ref. [27]						Calculated for interatomic distances from Ref. [28]					
	I–P		II–L		III–K		IV–P		V–L		VI–K	
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
$S_0 \rightarrow S_1$	4.74	0.209	4.45	0.180	4.68	0.188	4.74	0.063	4.46	0.195	4.68	0.067
$S_0 \rightarrow S_2$	4.91	0.267	4.72	0.260	4.86	0.292	5.06	0.341	4.73	0.262	4.99	0.348
$S_0 \rightarrow S_3$	5.86	0.418	5.74	0.766	5.84	0.477	5.89	0.741	5.74	0.738	5.86	0.771
$S_0 \rightarrow S_4$	6.05	0.028	5.94	0.095	6.09	0.028	6.17	0.106	5.95	0.109	6.18	0.108
$S_0 \rightarrow S_5$	6.35	0.674	6.25	0.264	6.31	0.627	6.53	0.240	6.25	0.261	6.45	0.251

Table 7. *Comparison of calculated and observed singlet-singlet transition energies, ΔE (in eV), and oscillator strengths, f, for 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine.*

Transition	Calculated for interatomic distances from Ref. [27]				Calculated for interatomic distances from Ref. [28]				Experiment [30]
	I–P		III–K		IV–P		VI–K		
6-Methylaminopurine									
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE
$S_0 \rightarrow S_1$	4.68	0.312	4.62	0.269	4.69	0.072	4.63	0.069	4.65–4.66
$S_0 \rightarrow S_2$	4.77	0.202	4.72	0.250	4.91	0.382	4.84	0.395	
$S_0 \rightarrow S_3$	5.75	0.328	5.73	0.372	5.78	0.651	5.75	0.670	
$S_0 \rightarrow S_4$	6.00	0.006	6.03	0.014	6.13	0.122	6.13	0.140	
$S_0 \rightarrow S_5$	6.22	0.650	6.17	0.618	6.35	0.171	6.28	0.179	
6-Dimethylaminopurine									
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	
$S_0 \rightarrow S_1$	4.64	0.393	4.60	0.338	4.66	0.067	4.61	0.060	4.51
$S_0 \rightarrow S_2$	4.71	0.135	4.65	0.195	4.84	0.407	4.77	0.425	
$S_0 \rightarrow S_3$	5.68	0.290	5.68	0.327	5.72	0.598	5.70	0.616	
$S_0 \rightarrow S_4$	5.99	0.004	6.02	0.040	6.11	0.168	6.11	0.208	
$S_0 \rightarrow S_5$	6.16	0.625	6.11	0.577	6.28	0.126	6.22	0.111	

However, it is very interesting that the calculations with the use of the geometrical structure from Ref. [28] satisfactorily interpret the shifts of the x band in the 6-NH_2, 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine series. Experimental evidence [30] shows that the energies corresponding to the absorption maximum of this band in 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine are lower than in the case of 6-NH_2-purine. The calculated energies of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine relative to the corresponding energies in 6-NH_2-purine have the following values (in eV):

		6-$NHCH_3$-purine	6-$N(CH_3)_2$-purine
calculated using geometry from [27]	$S_0 \rightarrow S_1$	-0.06	-0.08
	$S_0 \rightarrow S_2$	-0.14	-0.21
calculated using geometry from [28]	$S_0 \rightarrow S_1$	-0.05	-0.07
	$S_0 \rightarrow S_2$	-0.15	-0.22
observed [30]	the x band	-0.1	-0.25

The numbers presented above deserve some comment at this point. The calculations with the use of the geometrical structure from Ref. [28] show that the energy of the $S_0 \rightarrow S_2$ transition corresponds to the x band in 6-NH_2, 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine. On the other hand, on the basis of the calculations with the geometry from Ref. [27], we see that it is mainly energy of the $S_0 \rightarrow S_1$ transition that should be attributed to the maximum position of the x band in these purines. From a comparison of the results presented above it is seen that the former calculations are more satisfactory than the latter.

We have then generally found (for all purines studied) better agreement between theory and experiment by using in the calculations the geometrical structure of molecules under study from the paper by Stewart and Jensen [28]. Table 8 collects the first ten singlet-singlet transition energies, corresponding oscillator strengths and polarization of transitions calculated by the use of the latter geometry for purine, 6-NH_2, 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine. For the purpose of comparison in Table 8 we give the same theoretical quantities calculated by the use of the geometrical structure of molecules from Ref. [27].

Turning once more to the results of calculations reported in Table 6, we shall compare the adenine spectrum calculated with the use of the II–L and of the V–L sets of the β_{pq} values. It is evident, that either of these approaches gives the same values of the singlet-singlet transition energies. These two approaches differ only in the geometrical structures of the adenine molecule used for the calculation of the γ_{pq} integrals (and f-values). All values of the β_{pq} integrals were the same in either case. Therefore, it may be supposed that only the changes in the β_{pq} integral values used can influence the resulting transition energies more seriously. Consequently, the choice of the geometrical structure of the molecule for the calculations may be expected to exert no serious effect on the calculated transition energies and other theoretical results such as the π-electronic charge densities, π-bond orders, ionization potential and some other quantities. Therefore, if we refer to the Spencer or Stewart and Jensen geometry it should be remembered that, practically, we mean the actual choice of the β_{pq} integral values for the calculations.

Table 8. *Transition energies, ΔE (in eV), oscillator strengths, f, transition moment directions, α (in degrees), and polarization of transitions, Θ (in degrees), calculated for purine, 6-amino, 6-methylamino and 6-dimethylaminopurine. Comparison with experimental data*

Calculated for interatomic distances from Ref. [27] (the III-K set of β_{pq})				Calculated for interatomic distances from Ref. [28] (the VI-K set of β_{pq})				Experiment[a]	
ΔE	f	α	Θ[b]	ΔE	f	α	Θ[b]		$\Delta E(f)$
Purine									
4.801	0.095	-133	+47	4.713	0.101	-107	+73	4.71	4.68
5.182	0.159	-145	+35	5.296	0.099	+179	+1		~5.2
6.038	0.729	-78	-78	6.173	0.762	+107	-73		6.20
6.539	0.338	-95	+85	6.548	0.497	+60	+60		6.59
6.794	0.073	-14	-14	6.825	0.104	-105	+75		
6.955	0.301	-54	-54	6.931	0.264	+22	+22		
7.078	0.526	-153	+27	7.114	0.406	+158	-22		
7.800	0.082	+152	-28	7.739	0.007	+155	-25		
8.366	0.373	-5	-5	8.287	0.116	+147	-33		
8.598	0,279	+28	+28	8.634	0.353	+21	+21		
6-Aminopurine									
4.680	0.188	-159	+21	4.681	0.067	-158	+22	4.61 (10^{-3})	4.76
4.860	0.292	-136	+44	4.987	0.348	+29	+29	4.73 (0.27)	
5.844	0.477	+122	-58	5.859	0.771	+117	-63	5.98 (0.40)	
6.087	0.028	+7	+7	6.175	0.108	-153	+27		
6.305	0.627	-74	-74	6.452	0.251	+104	-76	6.77 (0.26)	
6.755	0.102	-137	+43	6.706	0.369	-151	+29		
6.958	0.261	-151	+29	6.894	0.108	-174	+6		
7.383	0.327	-146	+34	7.368	0.244	-121	+59	7.56 (-)	
7.863	0.169	-19	-19	7.916	0.002	-55	-55		
7.993	0.550	-2	-2	8.119	0.549	+175	-5		
6-Methylaminopurine									
4.625	0.269	+20	+20	4.632	0.069	+8	+8	4.66	
4.719	0.250	-131	+49	4.836	0.395	-150	+30		
5.734	0.372	+131	-49	5.750	0.670	-58	-58		
6.032	0.014	+163	-17	6.132	0.140	-121	+59		
6.168	0.618	-74	-74	6.277	0.179	-67	-67		
6.727	0.127	-110	+70	6.696	0.344	-152	+28		
6.903	0.203	-157	+23	6.878	0.115	+149	-31		
7.327	0.425	-142	+38	7.282	0.365	-121	+59		
7.782	0.431	+163	-17	7.889	0.013	-29	-29		
7.884	0.294	+180	0	8.022	0.531	+173	-7		
6-Dimethylaminopurine									
4.597	0.338	+22	+22	4.605	0.060	-1	-1	4.51	
4.655	0.195	-124	+56	4.771	0.425	-149	+31		
5.677	0.327	+135	-45	5.701	0.616	-55	-55		
6.019	0.040	+129	-51	6.107	0.208	-104	+76		
6.114	0.577	-74	-74	6.219	0.111	-51	-51		
6.714	0.152	-101	+79	6.692	0.329	-154	+26		
6.883	0.188	-158	+22	6.870	0.132	+137	-43		
7.314	0.459	-141	+39	7.256	0.409	-123	+57		
7.745	0.543	+164	-16	7.883	0.030	-22	-22		
7.852	0.176	+4	+4	7.987	0.507	+172	-8		

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[a] For experimental data for purine and 6-aminopurine see Table 3 and for those for 6-methylamino and 6-dimethylaminopurine see Table 7.

[b] The following relations exist between the angles α and Θ: $\Theta = \alpha$ if $-90° \leqq \alpha \leqq +90°$, $\Theta = -180° + \alpha$ if $\alpha > +90°$, and $\Theta = 180° + \alpha$ if $\alpha < -90°$.

A comparison of the present results with the previous ones as obtained by other researchers may be made for the purine and adenine molecules only[2]. We have obtained a more satisfactory agreement of the calculated spectrum (singlet-singlet transitions) of purine with the experimental one than that obtained previously by Berthod *et al.* [7, 8]. As can be seen in Table 8, in the case of adenine we have also obtained a more satisfactory agreement between the calculated ΔE values and experimental data than that reported in other papers. It should be pointed out however, that Tanaka and Nagakura's results [9] for adenine are also in a very good agreement with the experiment.

As to the theoretically determined polarizations, it is shown in Table 8 that the first two lowest-lying transitions in adenine are almost parallel to the C_4–C_5 axis in the purine ring (calculations with the geometry from Ref. [28]). This is in contradiction to the suggestions of Callis *et al.* [37] and of Mason [30]. It is interesting that the calculations show the $S_0 \rightarrow S_1$ transition in purine to be longitudinally polarized in accordance with Mason's suggestion [30]. The same calculations for the $S_0 \rightarrow S_2$ transition gave polarization prependicular to that for the $S_0 \rightarrow S_1$ one, in accordance with the suggestion of Mason [30] and recent observation of Drobnik *et al.* [49] on the fluorescent polarization.

A few words on the calculations of the singlet-singlet transition energies for 6-F, 6-OCH_3 and 6-OH-purine should be said. In the theoretical treatment, the conjugation between the π-electrons of the substituents (here: –F, –OCH_3, –OH) and those of the parent molecule (here: purine) is sensitive in the first place to the value of the core integral W_X for the substituent atom and also to the length of the carbon-substituent bond (i.e. to the β_{CX} integral). For molecules having the same C–X lengths, or if the difference of the C–X distances are not significant (e.g. $r_{C-F} \approx r_{C-O} \approx r_{C-OCH_3} \approx r_{C-NR_1R_2}$), the conjugation effect should be well described by the core integral for the substituent. Therefore, various kinds of physico-chemical properties of monosubstituted molecules (e.g. 6-F, 6-OR, 6-NR_1R_2-purines or monosubstituted benzenes, cf. [17, 18]), in particular their electronic spectra, may be well explained in terms of a simple model, in which the strengths of donor substituents are described by a comparison of the ionization potentials of the substituents. As we know, the substituents can be classified as electron donors or electron acceptors with respect to the parent molecule. The –NR_1R_2 groups are strong donors (the NHR_1R_2 compounds have low ionization potentials), the –OH group is moderately strong. The fluorine atom probably has both donor and acceptor properties, the former being dominant [67]. Our previous paper on monosubstituted benzenes [18] showed that both spectroscopic evidence and a comparison of the ionization potentials of the X–H substituents give the same relative order for the donating effect of the substituents, namely $F < OH < OCH_3 < NH_2 < NHCH_3 < N(CH_3)_2$. The present study, a comparison of calculated singlet-singlet transition energies for purine and for 6-substituted purines, gives the same results for the relative strengths of these substituents.

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[2] Valdemoro and Fraga [48] have recently attempted to calculate the energy of the lowest singlet-singlet transition for 6-NH_2, 6-$NHCH_3$ and 6-$N(CH_3)_2$-purine. The following energies (in eV) and oscillator strengths (in parentheses) for these purines have been calculated: 5.5 (0.80), 5.2 (1.30) and 5.1 (1.59).

It is seen from Table 9 that the divergence between the experimental and theoretical singlet-singlet transition energies for 6-OH and 6-OCH_3-purine is, in general, not larger than 0.2—0.3 eV. Thus we obtain good agreement of the calculated transition energies with the experiment. Unfortunately, there are no experimental data for the electronic spectrum of 6-fluoropurine. It would be of particular interest to have experimental information on the transition energies in this compound. Calculated transition energies for purine and 6-F-purine (Tables 5 and 9) have similar values. The calculated oscillator strengths for the $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ transitions in these compounds have also similar values. As to the first two transitions, it is seen that (contrary to the f-values for purine) the $S_0 \rightarrow S_1$ transition in 6-F-purine is weaker than the $S_0 \rightarrow S_2$ one. Thus it appears that the 6-F-purine absorption spectrum should be practically the same as the one for purine with the exception of the 2600–2400 Å region. As mentioned before, the purine spectrum shows a strong absorption band at 2600 Å and a shoulder at about 2400 Å. Contrary to this, the 6-F-purine spectrum (to be observed in future experiments!) should have a weak band (shoulder?) at about 2600 Å and a strong band at about 2400 Å. Turning once more to our previous correlation among the absorption bands od purines [1] it should be now evident that the strong absorption band in 6-F-purine at ~2400 Å correlates with the shoulder at ~2400 Å in the purine spectrum. On the other hand, the weak band at 2600 Å

Table 9. *Comparison of calculated and observed singlet-singlet transition energies, ΔE (in eV), and oscillator strengths, f, for 6-fluoro, 6-hydroxy and 6-methoxypurine. For the parameters used in the calculations see Tables 1 and 2*

Transition	Calculated for interatomic distances from Ref. [27]		Calculated for interatomic distances from Ref. [28]				Experiment
	I–P		IV–P		VI–K		
	ΔE	f	ΔE	f	ΔE	f	ΔE
6-Fluoropurine							
$S_0 \rightarrow S_1$	4.85	0.114			4.76	0.068	
$S_0 \rightarrow S_2$	5.20	0.176			5.35	0.145	
$S_0 \rightarrow S_3$	6.01	0.650			6.10	0.823	
$S_0 \rightarrow S_4$	6.61	0.258			6.66	0.473	
$S_0 \rightarrow S_5$	6.68	0.098			6.72	0.106	
6-Hydroxypurine							
$S_0 \rightarrow S_1$	4.83	0.123	4.81	0.051	4.74	0.057	4.98 [30]
$S_0 \rightarrow S_2$	5.13	0.246	5.34	0.225	5.26	0.234	
$S_0 \rightarrow S_3$	5.98	0.570	6.06	0.759	6.02	0.825	
$S_0 \rightarrow S_4$	6.38	0.049	6.44	0.251	6.44	0.218	
$S_0 \rightarrow S_5$	6.57	0.553	6.70	0.436	6.67	0.399	
6-Methoxypurine							
$S_0 \rightarrow S_1$	4.82	0.129	4.81	0.050	4.74	0.056	4.94 [33] 4.91 [30]
$S_0 \rightarrow S_2$	5.11	0.257	5.31	0.246	5.23	0.253	
$S_0 \rightarrow S_3$	5.96	0.545	6.04	0.757	6.00	0.822	6.20
$S_0 \rightarrow S_4$	6.32	0.058	6.39	0.237	6.38	0.204	6.53
$S_0 \rightarrow S_5$	6.55	0.591	6.70	0.436	6.66	0.390	

in the 6-F-purine spectrum will be correlated with the strong band at 2600 Å of the purine spectrum.

4.2. The Ground State Properties of Purines

In Table 10 are shown the π-electronic charge densities, π-bond orders and π-dipole moments calculated for the ground state of the molecules studied.

As we know, the π-electronic charge distribution may be used for the study of a number of properties of a molecule, e.g. the relative basicities of nitrogens, the position of the aromatic substitution [3], the chemical shifts of the protons.

For purine, we find (see Table 10) the relative order of the electron densities on nitrogens $N_7 > N_3 > N_1$ and on unsubstituted carbons $C_8 > C_6 > C_2$. In the case of adenine we find the order $C_8 > C_2$ for the π-electronic densities on carbons. The relative order of the π-electronic densities on nitrogens in adenine seems to be of interest. We find the orders $N_7 > N_1 > N_3$ and $N_1 > N_3 > N_7$ in case when the geometrical structure of adenine determined by Spencer and by Stewart and Jensen respectively were used in the calculations.

Dekker's evidence [51], for example, indicates that the site of protonation in adenine is N_1 (cf. also [52]). This conclusion has been confirmed by x-ray diffraction of 9-methyladenine-hydrobromide [53] (see also e.g. [54]). The site of protonation has been found to be at N_1 also in adenosine [55]. On the other hand, the results of alkylation of adenine and adenosine are not always so clear-cut, because this may depend on the reaction conditions. Adenine is alkylated at N_3 [56], whereas adenosine is alkylated at N_1 [57].

Thus, from experimental evidence it is known that the protonation occurs at the N_1 position of adenine, in accordance with the π-electronic charge densities at nitrogens obtained by the use of the Stewart and Jensen geometry in the calculations. However, it has been shown by Nakajima and Pullman [58], that the basicities in heterocycles containing nitrogen atoms (more than one) cannot be considered to be a function of the charge densities only. Therefore, from the fact that protonation occurs at the N_1 position of adenine, we cannot conclude about the correctness of our results mentioned above. For example, Veillard and Pullman [59] and Berthod *et al.* [6] have obtained a relative order of the π-electronic charge densities $N_7 > N_3 > N_1$. Our results with the use of the geometry from Ref. [27] is in accordance with that. It was shown by these authors that the basicities determined by a more complex function than the π-electronic charges of the nitrogens give an excellant agreement between the calculated and the observed basicities. By this procedure it was possible to predict the position of the most basic nitrogens in a large series of purines.

It may be added that the results for the π-electronic densities on the carbons, $C_8 > C_2, C_6$ for purine and $C_8 > C_2$ for adenine, are in agreement with the proton magnetic resonance studies[4] (see e.g. [62, 63]).

Table 11 contains the calculated energies of the highest occupied and of the lowest vacant m.o. of the molecules considered. The figures in parentheses are the ionization potentials of these molecules calculated with respect to the benzene molecule.

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[3] Cf. discussions concerning the chemical reactivity of the purine molecule [50].

[4] The original assignments of the C-protons in purine itself [60] were shown to be incorrect by several researchers [61].

Table 10. *The π-electronic charge densities (q_i), π-bond orders (p_{ij}) and π-dipole moments (μ in D) calculated for the ground state of purine, 6-aminopurine, 6-methylaminopurine and 6-dimethylaminopurine. π-dipole moment directions measured with respect to the x axis (see Figure) are given in parentheses. For the parameters used in the calculations see Tables 1 and 2 (the III–K and VI–K sets of β_{pq})*

	Calculated for interatomic distances from Refs.			Calculated for interatomic distances from Refs.	
	[27]	[28]		[27]	[28]
Purine					
q_1	1.234	1.220	p_{12}	0.603	0.580
q_2	0.813	0.806	p_{23}	0.702	0.726
q_3	1.249	1.242	p_{34}	0.554	0.532
q_4	1.005	0.991	p_{45}	0.607	0.628
q_5	0.987	0.982	p_{49}	0.412	0.416
q_6	0.833	0.882	p_{56}	0.573	0.572
q_7	1.288	1.252	p_{57}	0.436	0.400
q_8	0.958	0.953	p_{61}	0.697	0.713
q_9	1.633	1.671	p_{78}	0.777	0.819
μ	2.89 (132°)	2.68 (136°)	p_{89}	0.531	0.480
6-Aminopurine					
q_1	1.289	1.309	p_{12}	0.610	0.583
q_2	0.809	0.800	p_{23}	0.699	0.726
q_3	1.281	1.283	p_{34}	0.533	0.504
q_4	1.010	0.997	p_{45}	0.628	0.656
q_5	1.012	1.027	p_{49}	0.414	0.418
q_6	0.896	0.888	p_{56}	0.514	0.504
q_7	1.296	1.260	p_{57}	0.446	0.411
q_8	0.972	0.968	p_{61}	0.628	0.638
q_9	1.630	1.667	p_{78}	0.769	0.811
q_{10}	1.804	1.801	p_{89}	0.533	0.483
μ	1.76 (187°)	1.65 (198°)	$p_{10,6}$	0.458	0.465
6-Methylaminopurine					
q_1	1.303	1.324	p_{12}	0.612	0.585
q_2	0.807	0.800	p_{23}	0.698	0.725
q_3	1.289	1.291	p_{34}	0.527	0.499
q_4	1.011	0.998	p_{45}	0.633	0.661
q_5	1.018	1.032	p_{49}	0.415	0.419
q_6	0.910	0.904	p_{56}	0.501	0.490
q_7	1.299	1.262	p_{57}	0.449	0.414
q_8	0.976	0.971	p_{61}	0.611	0.620
q_9	1.630	1.667	p_{78}	0.766	0.809
q_{10}	1.756	1.751	p_{89}	0.533	0.484
μ	1.72 (193°)	1.81 (214°)	$p_{10,6}$	0.506	0.514
6-Dimethylaminopurine					
q_1	1.309	1.331	p_{12}	0.603	0.586
q_2	0.807	0.799	p_{23}	0.697	0.725
q_3	1.293	1.295	p_{34}	0.524	0.496
q_4	1.012	0.999	p_{45}	0.635	0.664
q_5	1.021	1.035	p_{49}	0.416	0.419
q_6	0.918	0.912	p_{56}	0.494	0.484
q_7	1.300	1.264	p_{57}	0.450	0.416
q_8	0.978	0.973	p_{61}	0.603	0.611
q_9	1.629	1.666	p_{78}	0.765	0.808
q_{10}	1.733	1.727	p_{89}	0.533	0.485
μ	1.76 (201°)	1.91 (221°)	$p_{10,6}$	0.528	0.536

Pullman and Rossi [64] have recently calculated the ionization potentials of the π- and lone-pair electrons of the nucleic acid bases, among them for adenine. A value of 8.4 eV for the π-electron ionization potential of adenine has been obtained by these researchers (cf. also [12, 65]). Our results for adenine are practically the same as those of Pullman and Rossi.

It may be added that our calculations predict a smaller value of ionization potential of a 6-X-purine than that of purine itself. In the series of 6-X-purines the order of decreasing values of molecular ionization potentials is the same as that of ionization potentials of the X–H substituents.

Table 11. *Electron-donor and electron-acceptor properties of purines. The calculated values of ionization potentials of purines are given in parentheses. All data in eV. (a) Calculated with the use of the Spencer geometry* [27], *III–K.* (*b*) *Calculated with the use of the Stewart and Jensen geometry* [28], *VI–K*

Compound	Energy of highest occupied m.o.		Energy of lowest vacant m.o.	
	(a)	(b)	(a)	(b)
Purine	−10.08 (8.97)	−10.47 (9.36)	−1.87	−2.02
6-OH-purine		− 9.98 (8.87)		−1.65
6-OCH$_3$-purine		− 9.92 (8.81)		−1.62
6-NH$_2$-purine	− 9.34 (8.23)	− 9.51 (8.40)	−1.54	−1.47
6-NHCH$_3$-purine	− 9.09 (7.98)	− 9.23 (8.12)	−1.45	−1.37
6-N(CH$_3$)$_2$-purine	− 8.98 (7.87)	− 9.10 (7.99)	−1.41	−1.33

Finally, we remark that the results of the present calculations and some other previous results [17—19] indicate that the semiempirical Pariser-Parr-Pople method can be satisfactorily used to interpret the electronic spectra and the basic ground-state properties of the conjugated systems containing the simple electron donor groups. It seems also that the nature of the electronic transitions in purine and 6-X-purines has been elucidated. One should remember, however, that the use of calculated transition energies to predict the sequence of the excited electronic states seems to be a poorer method for their classification than experimental tests.

Acknowledgement. The author would like to thank a referee for drawing his attention to Ref. [47].

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