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Relationes

Electronic Structure and Spectra of Organic Molecules

Part IX. SCF MO CI Calculations for 2,6-Disubstituted Purines*

J. S. Kwiatkowski

Department of Experimental Physics, The Nicholas Copernicus University, Toruń, Poland

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Calculations of the singlet-singlet ($\pi \rightarrow \pi^*$ type) transitions of a series of 2,6-disubstituted purines are presented. The Pariser-Parr-Pople method is used throughout and the agreement with experiment is good. The effects of the 2-X and 6-X substituents on the purine spectrum are discussed.

In the present report we plan to discuss the electronic spectra of a number of 2,6-disubstituted purines[1]. Particularly our attention will be concerned with the effects of the 2-X and 6-X substituents on the purine spectrum.

Calculations

The interesting features of the electronic spectra of all the molecules so far considered will be interpreted on the bases of the theoretical results obtained by means of the Pariser-Parr-Pople type calculations [4]. For the details of the choice of the semiempirical parameters the reader is referred to our previous papers [2, 5].

We will only comment on the choice of the semiempirical core integral for the X substituents in which only one atom contributes two π-electrons to the conjugated system. Namely, for the simple donor group of this sort, we put

$$W_X = \langle \varphi_X | T(i) + U_X^{++}(i) | \varphi_X \rangle = -I(\text{X–H}) - \gamma_{XX},$$

where I(X–H) is the first ionization potential of the X–H substituents and γ_{XX} is the two-electron one-center Coulomb repulsion integral. The following values (in eV) of ionization potentials I(X–H) were used in the present calculations (see Ref. [5]): $I(\text{HO–H}) = 12.59$, $I(\text{NH}_2\text{–H}) = 10.15$, $I(\text{NHCH}_3\text{–H}) = 9.2$, $I[\text{N(CH}_3)_2\text{–H}] = 8.8$, $I[\text{N(C}_2\text{H}_5)_2\text{–H}] = 8.24$.

As to the excited states, the configuration interaction was admitted and the eighteen singly excited configurations were allowed to interact.

Results and Discussion

Table 1 contains the calculated values of the singlet transition energies, oscillator strengths and polarization of transitions, as well as the experimental values for transition energies as obtained by different researchers. The calculated

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* For Part VIII ("SCF MO CI Calculations for Hypoxanthine and Guanine Isomers") see Kwiatkowski, J. S.: Acta physica polon. **36** (1969), in press.

[1] In the recent two papers [1, 2] the results of the SCF MO CI calculations for 2,6-diaminopurine and 2,6-di(diethylamino)purine were reported. The electronic spectrum of the first compound has been also interpreted theoretically in the very recent study of Fischer-Hjalmars and Nag-Chaudhuri [3].

changes on excitation in the π-electron density at the central atom (nitrogen or oxygen) of substituents and π-dipole moments in excited singlet states of molecules in question are also listed in this table.

As it can be seen from the figures presented in Table 1, the calculated values of transition energies are in good agreement with the experimental data. Since the ultraviolet spectra of all alkyl derivatives of 2,6-diaminopurine (2,6-DAP) are similar to that of 2,6-DAP itself, detailed discussion of the transition energies in these molecules will be omitted here. The spectra of the purines under study will be discussed here with regard to the effects of the 2-X and 6-X substituents on the purine spectrum.

Basing our work on theoretical results as presented in Table 1 and those given in Ref. [5] we have made an attempt to explain some features of the electronic spectra of the purines we are interested in. In order to explain these features it is worthwhile to remind of the effect of the single 2-X or 6-X group on the purine spectrum. Namely, on the basis of the results for monosubstituted purines [5] the following conclusions may be drawn:

a) The substitution of the 2-X group in the purine nucleus causes the shifts of the x_1 and x_2 bands of purine towards longer wavelengths with respect to a position of these bands in unsubstituted purine. However, the first band displaces more than the second one.

b) The 6-X substituent does not shift the x_1 band too much, while the x_2 band is shifted much more.

An examination of the spectroscopic properties of 2,6-disubstituted purines shows that upon simultaneous substitution of the 2-X and 6-X groups in the purine nucleus both the x_1 and x_2 bands of purine are also shifted towards longer wavelengths. Moreover, as shown in Table 2, the lowering of the first and second transitions in 2,6-disubstituted purines with respect to corresponding transitions in purine itself are, in general, of the same order. Then, it may be said that the effects of the 2-X and 6-X group upon the first two absorption bands of purine are additive.

The similar conclusion may be drawn from a comparison of the changes on excitation in π-electronic charge densities (Δq) at central atom of substituents (see Table 1). At present, we have also carried out calculations of the Δq values for monosubstituted purines [10]. For instance, these calculations give the following values of the changes on excitation in π-electronic charge density at nitrogen atom of the amino group (Δq_{NH_2}):

		2-NH_2-purine	6-NH_2-purine
Excitation to the 1st singlet state	Δq_{NH_2}:	-0.200	-0.067
	δE [a]: (in eV)	0.33	0.03
Excitation to the 2nd singlet state	Δq_{NH_2}:	-0.134	-0.226
	δE [a]: (in eV)	0.11	0.31

[a] δE stands for the calculated shifts of the lowest two excited singlet states of purine under substitution (cf. Table 2).

Table 1. *2,6-Disubstituted purines – transition energies to the singlet states, ΔE (in eV); oscillator strengths, f; polarization of transitions, ϑ (in degrees); changes on excitation in the π-electronic charge densities at substituents, Δq; and π-dipole moments, μ_π (in Debye units)*

Theoretical							Experimental	
ΔE	f	ϑ[a]	Δq(2-X)	Δq(6-X)	μ_π[b]	α[a]	ΔE	
2,6-Dihydroxypurine								
4.59	0.088	+47	−0.054	0.000	2.98	+ 32	4.64 [6]	
5.19	0.212	+45	−0.016	−0.066	1.06	− 7		
5.90	0.940	−62	−0.041	−0.017	2.30	− 22		
6.40	0.208	+ 1	−0.014	−0.176	2.05	+153		
6.49	0.245	−78	−0.076	−0.036	1.06	+ 44		
2,6-Diaminopurine								
4.38	0.114	+35	−0.141	−0.001	3.06	− 6	4.43 [6, 8]	4.43 [7]
4.91	0.305	+58	−0.043	−0.153	3.74	− 97	5.02	5.12
5.61	0.996	−47	−0.140	−0.176	4.99	− 97		5.77
5.99	0.023	+55	−0.145	−0.083	2.34	− 27		
6.15	0.238	−68	−0.159	−0.077	2.39	− 27		6.14
2,6-Dimethylaminopurine								
4.25	0.117	+32	−0.199	+0.013	3.80	− 23	4.35 [8]	
4.75	0.341	+62	−0.044	−0.179	5.20	− 99	4.98	
5.40	0.893	−42	−0.195	−0.228	6.00	−101	5.46	
5.84	0.002	−42	−0.161	−0.082	4.17	− 67		
5.96	0.241	−41	−0.315	−0.085	5.77	− 74		
2,6-Di(diethylamino)purine								
4.10	0.107	+30	−0.265	+0.038	5.02	− 36	4.22 [9]	
4.59	0.377	+66	−0.064	−0.191	6.74	− 99	~4.7	
5.20	0.822	−37	−0.212	−0.244	6.53	−102	5.06	
5.68	0.016	+75	−0.164	−0.132	5.25	− 86		
5.70	0.196	−26	−0.304	−0.175	7.76	−101		
2-Dimethylamino-6-aminopurine								
4.17	0.120	+40	−0.261	+0.028	5.38	− 26	4.23 [8]	
4.82	0.339	+75	−0.111	−0.135	5.47	− 80	4.98	
5.48	0.919	−39	−0.184	−0.255	5.32	− 96	5.49	
5.83	0.055	−58	−0.202	−0.047	5.11	− 39		
5.94	0.152	−48	−0.289	−0.111	6.29	− 70		
2-Amino-6-dimethylaminopurine								
4.37	0.109	+23	−0.114	−0.027	1.73	− 5	4.38 [8]	
4.73	0.356	+51	−0.016	−0.232	5.01	−127	4.86	
5.47	0.873	−46	−0.204	−0.206	6.02	−107	5.45	
5.90	0.018	−56	−0.145	−0.140	3.19	− 93		
6.10	0.355	−82	−0.031	−0.043	3.45	+ 53		

[a] The transition moment direction (ϑ) and dipole moment direction (α) are measured positive towards C_6 with respect to an axis from C_4–C_5 (see Ref. [5]).

[b] The π-dipole moments (in Debye units) in the ground state of the molecules under study were calculated as follows (the dipole moment directions in degrees are given in parenthesis): 2,6-diOH-purine: 1.23 (+44); 2,6-diNH_2-purine: 0.35 (+1); 2,6-di$NHCH_3$-purine: 0.47 (−82); 2,6-di$N(C_2H_5)_2$-purine: 1.09 (−105); 2-$N(CH_3)_2$-6-NH_2-purine: 0.84 (−42); 2-NH_2-6-$N(CH_3)_2$-purine: 0.41 (−164).

As we see, both the great bathochromic shift of the x_1 band of purine under substitution of the 2-NH_2 group and similar shift of the x_2 band of purine under substitution of the 6-NH_2 group, are accompanied by the great values of the π-electronic charge transfered from the substituents to the purine ring. Then, it may be concluded that the first absorption band in 2-NH_2-purine has more of the character of the *charge-transfer* (CT) band than its second band. On the contrary, in the case of 6-NH_2-purine the 260 nm absorption band which corresponds to the second transition may be called the CT band rather than the first absorption band[2] (a shoulder at ~ 269 nm, see Ref. [5]).

Table 2. *The shifts (in eV) of the x_1 (263 nm, 4.7 eV) and x_2 (~ 240 nm, ~ 5.2 eV) bands of purine upon substitution at the 2nd or/and 6th positions*

	The shift of the x_1 band		The shift of the x_2 band	
	Calc.[a]	Exp.	Calc.[a]	Exp.
Purine	Ref.	Ref.	Ref.	Ref.
2-OH-	0.08	?	−0.04	?
2-NH_2-	0.33	0.6	0.11	0.1
2-$NHCH_3$-	0.51	?	0.22	?
2-$N(C_2H_5)_2$-	0.73	?	0.34	?
6-OH-	−0.03	?	0.04	?
6-NH_2-	0.03	?	0.31	0.5
6-$NHCH_3$-	0.08	?	0.36	0.5
6-$N(C_2H_5)_2$-	0.15	?	0.63	?
2,6-diOH-	0.12	0.07	0.11	?
2,6-diNH_2-	0.33	0.28	0.39	0.3
2,6-di$NHCH_3$-	0.46	0.36	0.55	0.2
2,6-di$N(C_2H_5)_2$-	0.61	0.49	0.71	0.5

[a] Theoretical results for 2-X-purine and 6-X-purine were taken from Ref. [5].

Simultaneous substitution of the amino groups at the second and sixth positions of the purine nucleus causes the similar bathochromic shifts of the x_1 and x_2 bands of purine. The results for Δq's, as presented in Table 1, show that these shifts are accompanied by the similar transfers of the π-electronic charge from substituents ($\Delta q_{2-NH_2} + \Delta q_{6-NH_2}$) to the purine ring. Then, the first two absorption bands of 2,6-DAP may be, in the same extent, called the CT bands. However, the first absorption band of the molecule corresponds to an electronic transition, for which π-charge transfers from the 2-NH_2 group to the ring, while on excitation to the second singlet state π-charge transfers to the ring, in the first place, from the 6-NH_2 substituent. A comparison of the Δq's values presented in Table 1 shows that the similar feature is observed for other 2,6-disubstituted purines.

As pointed out before, the ultraviolet spectra of all alkyl derivatives of 2,6-DAP are similar to that of 2,6-DAP itself. However, an examination of the spectra of

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[2] More detailed discussion on this subject will be given elsewhere.

these purines shows certain differences those can be correlated with the position of the alkyl groups. Alkylation of the 2-NH_2 group causes the shift of the near ultraviolet absorption band of 2,6-DAP towards longer wavelengths, while the next band is practically unshifted.

In contradiction to that, an alkylation of the 6-NH_2 group causes the variable shift of the near ultraviolet band in the purines (see Table 3 and Ref. [8]). However, it may be said that the alkylation of the 6-NH_2 substituent practically does not cause any shift of the first band of 2,6-DAP, while the second band is shifted considerably. As we can see from Table 3, the calculation reproduces the bathochromic shifts of the first two absorption bands of 2-NH_2-6-$N(CH_3)_2$-purine with respect to those of 2,6-DAP. However, it should be added that if the similar calculations were performed for other 2-NH_2-6-alkylaminopurines, the calculation results would not reproduce the observed shifts of the absorption spectra.

Table 3. *Positions (in eV) of the first two absorption bands in some alkyl derivatives of 2,6-diaminopurine* [8]. *The calculated band positions are given in parenthesis for a comparison*

Purine	1st band	2nd band
2-NH_2-6-NH_2-	4.43 (4.38)	5.02 (4.91)
2-$NHCH_3$-6-NH_2-	4.34	5.00
2-NH(n-C_4H_9)-6-NH_2-	4.34	5.00
2-$N(CH_3)_2$-6-NH_2-	4.23 (4.17)	4.98 (4.82)
2-NH_2-6-$NHCH_3$-	4.52	4.8 [a]
2-NH_2-6-NH(n-C_4H_9)-	4.35	4.88
2-NH_2-6-$N(CH_3)_2$-	4.38 (4.37)	4.86 (4.73)

[a] Point of inflection.

The final remarks concern the correlation between the absorption bands of the purines under consideration and those of purine itself. It is evident that the first absorption bands of 2,6-disubstituted purines correlate with the x_1 band at 263 nm (4.7 eV) of purine, while the second bands correspond to a shoulder, the x_2 band at about 240 nm ($\sim$ 5.2 eV), of the purine spectrum. The correlation mentioned above is better illustrated in a figure. The reader is referred to our recent paper [11], which contains the correlation diagram between the excited singlet states of 2,6-disubstituted purines and those of purine itself.

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Dr. J. S. Kwiatkowski
Katedra Fizyki Doświadczalnej
Uniwersytet M. Kopernika
Toruń 1, ul. Grudziądzka 5, Poland