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Electronic Spectrum of 2,6-Di(Diethylamino)Purine

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The assignments of the absorption bands in 2,6-di-(diethylamino)purine were conclusively made by a theoretical consideration.

Drobnik and Augenstein [2] have recently measured the absorption spectrum of 2,6-di(diethylamino)purine (DDEAP) in various solvents. They have observed the most intense absorption band at $\sim$2450 Å and a near ultra-violet one at about 2940 Å. The former has an inflection at $\sim$2630 Å on the long-wave side the nature of which is uncertain: it may be a separate band or just a vibrational structure connected with the main band. In order to clarify its nature, a theoretical approach by means of the Pariser-Parr-Pople method [9] is presented here. Another purpose of this note is to discuss the correlations between the absorption bands of both DDEAP and 2,6-diamino purine (DAP) and those of purine.

The method of calculation is similar to that used in our previous papers [4–6], in which the electronic spectra of organic molecules containing the simple donor groups (F, OR, NR_1R_2, where R, R_1, $R_2 = H$, CH_3, C_2H_5 etc.) were satisfactorily interpreted. The detailed values of the empirical parameters used in the present calculations may be found in the aforementioned papers. It should be added that the one-electron core integral $W_X = \langle \varphi_X | T(i) + U_X^{++}(i) | \varphi_X \rangle$ for the donor substituent $X = NH_2$ or $N(C_2H_5)_2$ was put to be equal to $-I(X\text{–}H) - \gamma_{XX}$. The values 10.15 and 8.24 eV were used for the ionization potentials $I(NH_2\text{–}H)$ and $I[N(C_2H_5)_2\text{–}H]$, respectively (cf. [4]). All two-centre two-electron integrals γ_{pq} $(p \neq q)$ were calculated by means of the Nishimoto-Mataga approximation. The eighteen singly excited configurations were allowed to interact. Only those excitations from the lowest occupied molecular orbital and those to the highest unoccupied m.o. were omitted.

The table contains the singlet-singlet transition energies, ΔE, oscillator strengths, f, and polarization directions calculated for DDEAP. For comparison we give the same theoretical quantities calculated for DAP and purine. As seen from the figures presented in the table, the calculated values of the transition energies are in a very good agreement with the experimental data.

The most important conclusion that can be drawn is that the inflection at $\sim$2630 Å ($\sim$4.7 eV) in the DDEAP absorption spectrum covers one electronic transition of $\pi \rightarrow \pi^*$ type. This fact is also confirmed by the calculated directions of the transition moment. Drobnik *et al.* [3] have more recently measured the polarization of the fluorescence of DDEAP as a function of excitation wavelength. Their measurements indicate that the transition moments of the 2940 and 2450 Å absorption bands in this compound are oriented almost perpendicular to each other. Our results support this conclusion, because we obtain a value of about 70° for the angle between these transition moments. Therefore, it seems justified to conclude that two transitions in DDEAP (and also in DAP) – the first and third one, but not the first and second one – are oriented almost perpendicular to each other.

On the basis of the results presented in the table and from a comparison of the absorption bands in 2,6-disubstituted purines [7, 8] we can draw the following conclusions:

Table. *Electronic spectra of purines*

Theoretical			Experimental
ΔE (eV)	f	θ[a]	ΔE (eV)
Purine[b]			
4.71	0.101	73	4.68[c]
5.30	0.099	1	~5.2
6.17	0.762	−73	6.20
6.55	0.497	60	6.59
6.83	0.104	75	
2,6-Diaminopurine			
4.38	0.114	35	4.43[d]
4.91	0.305	58	5.12
5.61	0.996	−47	5.77
5.99	0.023	65	
6.15	0.238	−78	6.14
2,6-Di(diethylamino)purine			
4.10	0.107	30	4.22[e]
4.59	0.377	76	~4.7
5.20	0.822	−37	5.06
5.68	0.016	75	
5.70	0.196	−36	

[a] The transition moment direction (angle θ in degrees) is measured positive towards C_6 with respect to an axis from C_4–C_5 (see [6]).

[b] The theoretical results are taken from Ref. [6]. All singly excited configurations were allowed to interact.

[c] In trimethyl phosphate [1].

[d] In H_2O, $pH = 6$ [7].

[e] In various solvents (methylcyclohexane, isopropanol, water) [2].

a) The 2940 Å (4.22 eV) and 2800 Å (4.43 eV) absorption bands of DDEAP and DAP respectively correlate with the x_1 absorption band at 2630–2650 Å (~4.7 eV) of purine itself.

b) The absorption bands at ~2630 Å (~4.7 eV) and 2420 Å (5.12 eV) in the disubstituted purines in question correspond to a shoulder (the x_2 band at ~2400 Å, ~5.2 eV) in the purine spectrum.

c) It is also evident that the absorption bands which correspond to the third transition in DDEAP and DAP correlate with the y band of purine at 2000 Å (6.20 eV).

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