THE ELECTRON-ACCEPTING STRENGTH OF NAD^+*

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The oxidized form of nicotinamide adenine dinucleotide (NAD^+) has been predicted to be a relatively strong electron acceptor because of its activities as a coenzyme and as a link in the respiratory cycle. The energy of its lowest empty molecular orbital[1] is $-0\cdot356\ \beta$, and the formation of charge-transfer (CT) complexes with indole derivatives[2] and reduced flavin mononucleotide[3] ($FMNH_2$) has been reported.

TABLE 1

CHARGE-TRANSFER ABSORPTIONS OF NAD^+–DONOR SYSTEMS

The I_D values quoted are from unpublished data. Uracil, guanine, and 2-thiouracil were too sparingly soluble to produce any observable effect

Donor	Donor Concn.	λ_{CT} (nm)	λ_{CT} (cm^{-1})	I_D (eV)	HOMO (β)	Solvent[a]
2-Amino-4,7-dihydroxy-6-methylpteridine	satd.	415	24100		[b]	A
2-Amino-4-hydroxy-6,7-dimethylpteridine	satd.	423	23600		[b]	A
Serotonin creatine sulphate	0·02M	320	31200		0·461[c]	B
Lysergic acid	0·02M	340	29400	7·8	[d]	B
Indole	satd.	310	32200	7·9	0·534[c]	B
Uric acid	satd.	340	29400	7·5	0·172[c]	B
Promazine hydrochloride	0·05M	380	26300	7·2	[e]	B
Promethazine hydrochloride	0·05M	385	25900	7·2		B
Methdilazine hydrochloride	0·02M	380	26300	7·2		B
Chlorpromazine hydrochloride	0·02M	390	25600	7·3		B

[a] A, 5N HCl; B, water buffered at pH 7·1.

[b] HOMO energy of 2-amino-4,7-dihydroxypteridine is $0\cdot387\ \beta$!

[c] From Szent-Gyorgyi, A., "Introduction to a Submolecular Biology." p. 38. (Academic Press: New York 1960.)

[d] HOMO of lysergic acid diethylamide (Szent-Gyorgyi, loc. cit.) is $0\cdot218\ \beta$.

[e] HOMO of phenothiazine is $0\cdot646\ \beta$ (Malrieu, J. P., and Pullman, B., *Theor. chim. Acta*, 1964, **2**, 293).

We have shown that NAD^+, of concentration $1\cdot03\times10^{-2}$M, when mixed with fairly strong electron donors, such as substituted pteridines, uric acid, serotonin creatine sulphate, lysergic acid, and phenothiazines, gave solutions which were coloured yellow to orange because of the formation of CT complexes.

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[1] Pullman, B., and Pullman, A., "Quantum Biochemistry." p. 518. (Interscience: New York 1963.)

[2] Isenberg, I., and Szent-Gyorgyi, A., *Proc. natn. Acad. Sci. U.S.A.*, 1959, **45**, 1229.

[3] Sakurai, T., and Hosoya, H. *Biochim. biophys. Acta*, 1966, **112**, 459.

The positions of the CT band maxima (λ_{CT}) are given in Table 1, together with the available ionization energies (I_D) and the energies of the highest occupied molecular orbitals (HOMO) of the donors. Since in most cases the CT absorption overlaps the donor absorption, the error in λ_{CT} is *c.* ± 5 nm.

The positions of λ_{CT} correlate reasonably with I_D, but not so well with the energies of the HOMO. This is not surprising in view of the approximations involved in the molecular orbital method.[4]

The *N*-substituted phenothiazine–*m*-dinitrobenzene systems, in chloroform, absorb at *c.* 450 nm (unpublished data). Therefore, by comparison, the electron affinity of NAD^+ is less than that of *m*-dinitrobenzene, i.e. less than 0·8 eV.[5]

The spectra were recorded on a Cary 14 spectrophotometer. The NAD^+ used was obtained from Sigma Chemical Company.

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[4] Streitwieser, Jr., A., "Molecular Orbital Theory for Organic Chemists." p. 33. (John Wiley: New York 1962.)

[5] Batley, M., Ph.D. Thesis, University of Sydney, 1966, p. 132.