
ON APPLICABILITY OF CNDO/S-CI METHOD TO CALCULATION OF ELECTRONIC SPECTRA. 1-METHYL-3-CARBAMOYLPIRIDINIUM CATION AND 1,4-DIHYDRONICOTINAMIDE*

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Further arguments have been gathered to support the applicability (as a variable) of the parameter κ fixed by del Bene and Jaffé in the CNDO/S method. For the heteroaromatic ion *I* the value 0.585 suggested by these authors is suitable, but for the 1,4-dihydropyridine derivative *II* agreement between experimental and a calculated spectrum can be obtained with $\kappa < 0.4$. Furthermore, effects of the optimum molecular geometry and width of the configuration interaction on the results of the theoretical treatment are discussed.

1-Methyl-3-carbamoylpyridinium cation (*I*) and 1-methyl-1,4-dihydrionicotinamide (*II*) belong to trivial bioorganic models of the coenzymes NAD^+ and NADH. As they represent (besides the adenine component) substantial part of chromophoric system of the coenzyme molecules, it is worth while to examine the corresponding electronic spectra. Besides their practical use for following the occurrence of the both coenzyme forms or their models the said spectral properties of the chromophoric subsystems were also studied theoretically by MO methods namely within the framework of the pi-electron approximation for the present. A good agreement between the calculated excitation energies of the $\pi \rightarrow \pi^*$ transitions and positions of experimental absorption bands was achieved for the compound *II* with the use of the PPP method¹. No studies involving all valence electrons have been published so far. As the molecules *I* and *II* contain, besides the pi-electrons, also free electron pairs at the amidic group, we were interested whether any transitions with participation of sigma electrons make themselves felt in the corresponding electronic spectra. So far most all-valence-electrons calculations of electronic transitions have obviously been carried out by the CNDO/S method published by del Bene and Jaffé^{2,3}. These authors found that for satisfactory agreement between the theoretical and the experimental excitation energies it is necessary (besides other less substantial modifications of the original CNDO/2 procedure) to introduce the empirical parameter $\kappa = 0.585$

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with which they multiplicatively all overlap integrals forming the pi-MOs. However, when the said α value was used in calculation of spectra of some components of nu-

TABLE I

Theoretically Calculated Spectral Characteristics of the Compound I for Two Considered CI Widths

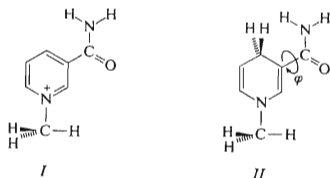
Band	16 Mono-excited configurations				36 Mono-excited configurations			
	λ_{\max} , nm (log <i>f</i>)				λ_{\max} , nm (log <i>f</i>)			
	$\alpha = 0.585$	$\alpha = 0.685$	$\alpha = 0.785$	$\alpha = 0.885$	$\alpha = 0.585$	$\alpha = 0.685$	$\alpha = 0.785$	$\alpha = 0.885$
A	369.4 (-3.257)	329.2 (-2.989)	284.7 (-2.650)	272.8 (-2.522)	380.6 (-3.311)	338.7 (-3.047)	308.6 (-2.831)	274.9 (-2.549)
B	264.3 (-2.348)	255.0 (-3.509)	245.5 (-3.342)	238.1 (-3.766)	272.4 (-3.737)	262.7 (-3.883)	252.8 (-4.143)	242.0 (-4.839)
C	263.9 (-0.843)	230.0 (-0.802)	203.2 (-0.768)	201.2 (-2.439)	264.6 (-0.833)	230.6 (-0.805)	208.7 (-2.988)	201.8 (-3.110)
D	225.3 (-1.838)	207.8 (-3.234)	190.7 (-1.880)	181.6 (-0.888)	228.6 (-3.366)	216.6 (-3.084)	204.3 (-0.798)	184.1 (-0.843)

TABLE II

Characteristics of Individual Transitions in Theoretically Calculated Spectrum of II

Band	16 Mono-excited configurations configuration				36 Mono-excited configurations configuration			
	(weight of configuration, %)				(weight of configuration, %)			
	$\alpha = 0.585$	$\alpha = 0.685$	$\alpha = 0.785$	$\alpha = 0.885$	$\alpha = 0.585$	$\alpha = 0.685$	$\alpha = 0.785$	$\alpha = 0.885$
A	1-2' (35)	1-2' (43)	1-2' (54)	1-2' (50)	1-2' (34)	1-2' (41)	1-2' (45)	1-2' (48)
B	1-1' (84)	1-1' (82)	1-1' (69)	1-1' (60)	1-1' (79)	1-1' (76)	1-1' (70)	1-1' (56)
C	2-1' (56)	2-1' (45)	2-1' (47)	4-1' (93)	2-1' (58)	2-1' (45)	5-1' (80)	4-1' (93)
D	3-1' (53)	1-4' (41)	2-1' (52)	2-1' (84)	1-4' (33)	5-1' (40)	2-1' (45)	2-1' (67)

cleic acids, a considerable discrepancy was found between theory and experiment^{4,5}. In a recent study Zahradník and coworkers⁶ found that the parameter must be changed for some molecules containing carbonyl group, and they give the value 0.858 as the most suitable for the studied substances. In this report we applied the CNDO/S method with variable parameter κ to the calculation of spectral characteristics of the chromophores *I* and *II*.



CALCULATIONS

All the calculations were carried out on an IBM 370/145 and an ICL-4-72 computers using the standard CNDO/S-CI program (by Dr Čárský). For the calculations we used the MO models of the energetically most stable conformers represented by the formulas *I* and *II* optimized with respect to all geometrical degrees of freedom^{7,8}. Besides, for the compound *II* we also studied the MO model partially optimized⁹ with respect to only the value of the torsion angle ϕ . For comparison with experimental data we used the calculated values of the maxima of the electronic bands λ_{\max} and the logarithms of the oscillator strength f . Numbering of the bonding MO's (1, 2, 3, ...) and the antibonding MO's (1', 2', 3', ...) started from the frontier orbitals HOMO and LUMO.

RESULTS AND DISCUSSION

The cation I. In aqueous solutions of its fluoride and tetrafluoroborate, electronic spectra of this chromophore show¹⁰ a single intensive absorption band with $\lambda_{\max} = 265$ to 266 nm and $\log \epsilon = 2.63$ to 2.62 with probable properties of the $\pi \rightarrow \pi^*$ absorption.

The CNDO/S-CI calculations were carried out for $\kappa = 0.585$ to 0.885 with the CI width of 16 or 36 mono-excited electronic configurations. Dependence of the calculated spectral characteristics of the near UV region ($\lambda > 200$ nm) on the varied parameter are given in Table I and Fig. 1. The calculation obviously predicts a single intensive long-wave band C with $\log f > -0.7$ in accordance with experimental¹⁰ envelope absorption curve. Furthermore, confrontation of the calculated λ_{\max} values shows that the best agreement between the experimental and the theoretical data is achieved at the value $\kappa = 0.585$ recommended by the authors^{2,3}. On the contrary, effect of the different CI width on the calculated characteristics of the mentioned absorption band is low ($\lambda_{\max} = 263.9$ nm, $\log f = -0.843$ for 16 configurations;

TABLE III
Character of the Individual Orbital Levels Calculated for the Compounds I and II

MO	Character of the level				MO	Character of the level			
	compound I		compound II			compound I		compound II	
	type	energy kJ mol ⁻¹	type	energy kJ mol ⁻¹		type	energy kJ mol ⁻¹	type	energy kJ mol ⁻¹
1	<i>n</i>	-1 326.1	π	- 889.0	1'	π^*	-552.0	π^*	-207.6
2	π	-1 340.3	<i>n</i>	- 939.8	2'	π^*	-475.2	π^*	-147.8
3	π	-1 390.1	π	-1 109.2	3'	π^*	-291.7	π^*	-100.7
4	π	-1 468.9	π	-1 116.0	4'	π^*	-189.7	σ^*	279.8
5	σ	-1 583.8	σ	-1 223.9	5'	σ^*	- 80.1	σ^*	340.4
6	σ	-1 659.8	σ	-1 306.8	6'	σ^*	- 16.0	σ^*	361.2

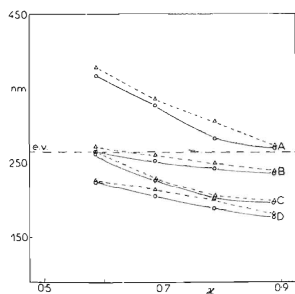


FIG. 1

Dependence of Position of the Theoretically Calculated Absorption Bands on the Chosen x Value for the Compound I

Full line denotes the calculation for 16 mono-excited configurations, dashed line — the calculation for 36 mono-excited configurations.

e.v. experimental value.

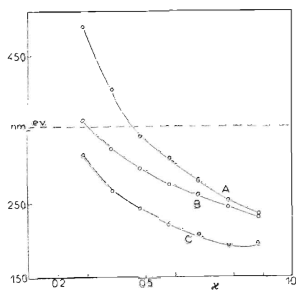


FIG. 2

Dependence of Position of the Theoretically Calculated Absorption Bands on the Chosen x Value for the Compound II

e.v. experimental value.

$\lambda_{\text{max}} = 264.6 \text{ nm}$, $\log f = -0.833$ for 36 configurations- for $\alpha = 0.585$ in the both cases). This band shows the $\pi \rightarrow \pi^*$ character with 56 and 58% weight respectively, of the electron configuration $1-2'$. Table II gives order and weights of the most significant electronic configurations in these optimum CNDO/S-CI calculations, and Table III presents the character of the individual orbital levels. From the data it follows unambiguously that the chromophoric system *I* shows characteristic properties of ultraviolet absorption of pyridinoid compounds, *i.e.* intensive maxima with marked demonstration of the configuration interaction between π and π^* MOs. Effect of electronic structure of amidic group only makes itself felt by forbidden or very little intensive absorption bands (*e.g.* A and B), and, therefore, it is not seen at all in the experimental absorption curve. In connection therewith it is worth mentioning that the CNDO/S-CI calculation gives the HOMO as σ or n with a marked contribution of free electron pairs at the oxygen atom, whereas the LUMO is unambiguously π^* . The corresponding $n \rightarrow \pi^*$ transition ($N \rightarrow V_1$) does not make itself felt significantly in the absorption spectrum for the above-mentioned reasons. however, it will obviously have indisputable significance for dispersion curve of NAD^+ and its models.

1,4-Dihydroderivative *II*. Electronic spectra of ethanolic and aqueous solutions of *II* show an intensive absorption band^{1,11,12} with $\lambda_{\text{max}} = 355$ and 360 nm and $\log \epsilon$ in the region 3 to 4. The CNDO/S-CI calculations were carried out for $\alpha = 0.285$ to 0.885 with the fixed CI width to 36 mono-excited electronic configurations. De-

TABLE IV
Theoretically Calculated Spectral Characteristics of Compound *II* before and after Full CNDO/2 Optimization of Geometry

Band	Original geometry ⁹								Geometry after full optimization ⁸
	$\lambda_{\text{max}}, \text{nm}$ ($\log f$)								$\lambda_{\text{max}}, \text{nm}$ ($\log f$)
	$\alpha = 0.285$	$\alpha = 0.385$	$\alpha = 0.485$	$\alpha = 0.585$	$\alpha = 0.685$	$\alpha = 0.785$	$\alpha = 0.885$	$\alpha = 0.285$	$\alpha = 0.385$
A	498.8 (-3.943)	406.7 (-3.943)	342.7 (-3.163)	313.7 (-3.054)	281.0 (-2.847)	255.6 (-2.674)	235.4 (-2.529)	496.6 (-4.043)	411.1 (-3.576)
B	364.7 (-1.112)	326.6 (-0.991)	300.2 (-0.902)	278.8 (-0.851)	262.0 (-0.788)	247.3 (-0.734)	234.1 (-0.687)	390.2 (-1.199)	352.7 (-1.036)
C	317.2 (-1.183)	268.3 (-1.194)	243.5 (-0.832)	223.1 (-0.638)	207.0 (-0.498)	193.5 (-0.386)	195.6 (-3.365)	331.4 (-1.026)	278.3 (-1.517)

pendences of the values of the calculated spectral characteristics of the partially optimized MO model of the chromophore *II* on the parameter κ are given in Fig. 2. The second longest-wave band B is obviously predicted as an intensive one with $\log f > -0.85$ and corresponds thus to the experimental absorption maximum^{1,11,12}. At the same time it is seen that agreement between the calculated and the found wavelength $\lambda_{\max} = 355$ nm cannot be achieved until the value $\kappa = 0.305$, *i.e.* lower than that recommended by del Bene and Jaffé^{2,3} and by Zahradnik and coworkers⁶. Therefrom it can be concluded that structural differences between the chromophoric systems of the compound *II* and the cation *I* would require further reparametrization in the CNDO/S-CI method, the problem of preliminary parameter assessment remaining hereafter obscure.* However, the CNDO/S-CI calculations were also carried out for the molecular structure *II* fully optimized⁸ with respect to all geometrical degrees of freedom, so that it might be verified that, in our case, the extremely low κ value is not due to bad geometry of the used MO model of *II*. From Table IV it follows that for $\kappa = 0.285$ and 0.385 the λ_{\max} and $\log f$ values are not markedly different, the "best" parameter $\kappa = 0.378$ obtained by interpolation for agreement between the calculated and the experimental wavelength $\lambda_{\max} = 355$ nm being again lower than that given by the authors^{2,3}. Although the effect of the de-

TABLE V

Characteristics of Individual Transitions in the Theoretically Calculated Spectrum of Compound *II* before and after Full CNDO/2 Optimization of Geometry

Band	Original geometry ⁹ configuration (weight of configuration, %)						Geometry after full CNDO optimization ⁸ (weight of configuration, %)		
	$\kappa = 0.285$	$\kappa = 0.385$	$\kappa = 0.485$	$\kappa = 0.585$	$\kappa = 0.685$	$\kappa = 0.785$	$\kappa = 0.885$	$\kappa = 0.285$	$\kappa = 0.385$
A	4-1' (52)	3-1' (56)	3-1' (59)	3-1' (58)	2-1' (61)	2-1' (66)	2-1' (71)	4-1' (54)	4-1' (59)
B	1-1' (92)	1-1' (93)	1-1' (94)	1-1' (95)	1-1' (96)	1-1' (96)	1-1' (97)	1-1' (92)	1-1' (94)
C	2-1' (68)	1-2' (80)	1-2' (87)	1-2' (91)	1-2' (93)	1-2' (94)	1-3' (96)	2-1' (71)	1-2' (58)

* It is evident that similar procedure could bring satisfactory agreement between the calculated and the experimental characteristics of the earlier mentioned^{4,5} nucleic bases, too.

tailed starting geometry is obvious to a certain extent, it cannot be considered a dominant factor decreasing the value of the parameter κ , the structural type of the given chromophore being evidently decisive.

Furthermore, the data of Table V show that the absorption band B, observed experimentally^{1,11,12} and used for identification of NADH or its bioorganic models, is due to practically "pure" $N \rightarrow V_1$ transition with the weight of the $1-1'$ configuration above 90%, which contrasts with the situation of the cation *I*. In Table III it is noteworthy that order of the orbital levels of the chromophores *I* and *II* is different. In the case of the 1,4-dihydropyridine derivative *II* the HOMO and the LUMO are of the π type, so that the $\pi-\pi^*$ excitation causing the existence of the band B is most significant for both absorption and fluorescence. Also noteworthy is the calculated longest-wave band A with λ_{\max} about 410 nm and $\log f < -3.4$ (evidently forbidden in the absorption spectrum) which could affect the shape of the dispersion curves of the chromophores type *II*. The highest weight in this excitation has the configuration $4-1'$ in which the electrons are excited from the bonding MO localized at the heteroatoms of amidic group to the antibonding π^* -MO which is in fact delocalized to the heterocyclic ring. Hence the band A is due to the presence of the said substituent.

On the whole the results show that, in contrast to the PPP method used successfully in similar systems¹³, the CNDO/S-CI method cannot hereafter be considered standard due to the uncertainty in the choice of the empirical parameter κ .

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