QUANTUM-CHEMICAL INTERPRETATION
OF ELECTRONIC ABSORPTION SPECTRA
OF THE HANTZSCH 1,4-DIHYDROPYRIDINES*

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Electronic absorption spectra of 1,4-dihydropyridines *I—XII* have been interpreted by means of the SCF–PPP method. Possibility of interpretation of the said spectra of 4-substituted derivatives *V—XII* as superposition of two independent chromophoric systems is discussed.

Molecules of 1,4-dihydropyridines contain a characteristical chromophoric system, so their electronic absorption spectra are used for their identification[1,2]. Theoretical interpretations of positions and intensities of the absorption bands by the PPP method were satisfactory for the simplest dihydropyridines[3], whereas with the more complex dihydronicotinamides they gave worse results[4]. A better similarity of the calculated and experimental spectra was reached with the use[5] of a parametrization involving also the non-conjugated parts of the molecules. Effects of parametrization and of the model used on relation between the calculated and the measured absorption bands in electronic spectra of 3,5-dicyano-1,4-dihydropyridine and 3,5-dicyano-1,2-dihydropyridine were studied in detail[6]. The present communication tries to carry out an analogous interpretation of electronic absorption spectra of structurally more complicated 1,4-dihydropyridines *I—XII*.

MEASUREMENTS AND CALCULATIONS

The compounds *I—XII* were prepared by the modified Hantzsch synthesis[7], and their melting points corresponded to the values published[7–15]. The electronic absorption spectra of ethanolic solutions ($4 . 10^{-5}$ mol l^{-1}) of the compounds *I—XII* were measured with a Specord UV-VIS apparatus. The spectra of mixtures of the compounds *I—IV* with *o*-nitrotoluene were measured in ethanolic solutions with concentrations $4 . 10^{-5}$ mol l^{-1} of each component. The obtained spectral characteristics of the compounds *I—XII* are given in Table I. For the SCF–MO–LCAO calculations we chose the original PPP procedure[16–18] involving sixteen monoexcited configurations and approximation of bicentric repulsion integrals according to Mataga and Nishimoto[19]. The calculations were carried out with an IBM-370 computer using the standard program. On the

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basis of previous experience[6,20] we chose for the calculation the hyperconjugation model[6] of methylene and methyl groups in molecules of the studied dihydropyridines. Geometry of the calculated structures was derived from the ideal C—C bond lengths (140 pm) and angles (120°) except for the following bonds: $C(sp^2)$—$C(H_3)$ 154 pm; $C(sp^2)$—$C(sp)$ 146 pm; $C{\equiv}H_3$ or $C{=}H_2$ 45 pm; $C(sp)$—$N(sp)$ 116 pm; $C(sp^2)$—$O(sp)$ 120 pm; $C(sp^2)$—$O(sp^2)$ 135 pm; $N(sp^2)$—$O(sp)$ 124 pm; $C(sp^2)$—$N(O_2)$ 148 pm. The parameters used in the PPP calculations are given in Table II.

RESULTS AND DISCUSSION

UV spectra of the studied compounds I—XII show two absorption maxima, the longer-wave one in the region 300—400 nm and the shorter-wave one in the region 200—300 nm (Table I). The spectra of compounds I—IV are simpler than those of the 4-substituted derivatives V—XII. The spectrum of dicyano derivative I only shows the two mentioned maxima. The spectra of diesters III and IV show an indication of splitting of the shorter-wave band into three bands which are quite distinct in the spectrum of diketone II. In contrast to the spectrum of compound I, those of the 4-substituted dicyano derivatives V and IX show an indication of splitting of the shorter-wave band into two bands. The absorption curves of the other 4-substituted derivatives VI—VIII and X—XII show three absorption maxima and (in the spectra of X—XII) a slight indication of a fourth band. Results of the PPP calculations of electronic absorption spectra of compounds I, II and IV and their comparison with experiment are given in Table III.
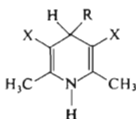
I, R = H, X = CN

II, R = H, X = COCH$_3$

III, R = H, X = COOCH$_3$

IV, R = H, X = COOC$_2$H$_5$

V, R = C$_6$H$_5$, X = CN

VI, R = C$_6$H$_5$, X = COCH$_3$

VII, R = C$_6$H$_5$, X = COOCH$_3$

VIII, R = C$_6$H$_5$, X = COOC$_2$H$_5$

IX, R = o—NO$_2$C$_6$H$_4$, X = CN

X, R = o—NO$_2$C$_6$H$_4$, X = COCH$_3$

XI, R = o—NO$_2$C$_6$H$_4$, X = COOCH$_3$

XII, R = o—NO$_2$C$_6$H$_4$, X = COOC$_2$H$_5$

Compounds I—IV: In the case of the dicyano derivative I, the calculated values (Table III) allow a relatively good interpretation of both its spectral bands. Position of the longer-wave band is well predicted by calculation, the short-wave band being a superposition of several bands. The calculated band coresponding to $1—2'$

TABLE I

Electronic spectra of compounds $I-XII$

Compound	λ_{max}, nm (log ε)			
I	346·7 (4·03)	—	—	220·1 (4·40)
II	408·2 (3·97)	275·3 (4·02)[a]	250·0 (4·23)	204·8 (4·09)
III	370·4 (4·07)	250·0 (4·17)[a]	230·8 (4·33)	203·4 (4·05)[a]
IV	370·4 (4·08)	252·1 (4·19)[a]	230·8 (4·36)	204·1 (4·16)[a]
V	342·8 (3·96)	—	239·1 (3·85)[a]	217·4 (4·34)
VI	379·9 (4·07)	—	260·9 (4·23)	209·8 (3·57)
VII	355·0 (4·06)	—	250·0 (4·31)	206·2 (4·29)
$VIII$	357·7 (4·10)	—	239·0 (4·36)	209·8 (3·90)
IX	333·3 (3·88)	—	251·9 (4·08)[a]	218·8 (4·42)
X	384·6 (3·89)	322·6 (3·78)[a]	253·2 (4·36)	213·1 (4·35)
XI	327·9 (3·86)	285·7 (3·86)[a]	236·3 (4·32)	205·3 (4·34)
XII	333·3 (3·93)	—	237·1 (4·43)	212·9 (4·41)

[a] Inflection.

TABLE II

The standard parametrization used in the PPP calculations

Atom	Ip, eV	A, eV	Ref.	Bond	E^a	Ref.
$C(sp^2)$	11·16	0·03	19	$C(sp^2)—C(sp)$	0·90	6
$C(sp^2)^b$	12·40	0·72	24	$C(sp^2)—CH_3$	0·51	6
$C(sp)$	11·19	0·10	19	$C(sp^2)—CH_2$	0·40	6
$C(H_3)$	11·42	0·58	6	$C(sp^2)—N(sp^2)^c$	0·80	6
$C(H_2)$	11·42	0·58	6	$C(sp^2)—N(sp^2)^f$	0·94	24
$N(sp^2)^c$	27·50	9·20	21	$C(sp^2)—O(sp^2)$	0·80	23
$N(sp^2)^d$	20·40	5·51	24	$C(sp^2)—O(sp)$	1·00	23
$N(sp)$	14·18	1·66	19	$C≡H_3$, $C≡H_2$	1·25	6
$O(sp^2)$	32·90	10·00	23	$C(sp)—N(sp)$	1·40	22
$O(sp)^e$	13·60	2·30	23	$N(sp^2)—O(sp)$	1·14	24
$O(sp)^d$	10·80	4·30	24	$O(sp^2)—CH_3$	0·45	23
$H_3(C)$	9·50	0·00	21	$O(sp^2)—CH_2$	0·32	23
$H_2(C)$	9·50	0·00	21			

[a] In β units ($\beta = -2·388$ eV); [b] the atom to which nitro group is bound; [c] in dihydropyridine ring; [d] in nitro group; [e] in carbonyl group; [f] the $C—NO_2$ bond.

transition seems to have much too long wave length. The calculation of spectra of compounds $II-IV$ considered three possible mutual orientations (in plane) of $C=O$ bonds in the 3,5-substituents (see formulae a, b, c). Structural studies

TABLE III

The SCF–MO–LCAO-calculated absorption bands of 1,4-dihydropyridines $I-IV$

Model	λ_{max}, nm	log f	$i-j^a$	Weight, %	λ_{max}, nm	log f	$i-j^a$	Weight, %
I	345·5	−0·68	1−1′	99	270·0	−0·57	1−2′	87
	227·3	0·07	2−1′	82	215·6	−0·57	3−1′	73
	214·1	−1·92	1−3′	94	209·4	−0·97	1−4′	86
IIa	401·1	−0·90	1−1′	98	300·4	−0·64	1−2′	87
	249·6	−0·05	2−1′	71	242·4	−2·54	3−1′	69
	234·0	−2·84	2−2′	55	227·2	−0·17	1−3′	67
	226·9	−1·13	1−4′	72	222·2	−1·45	4−1′	46
IIb	393·9	−0·68	1−1′	97	294·7	−0·61	1−2′	92
	256·9	−0·38	2−1′	77	238·0	−0·90	2−2′	64
	230·1	−2·11	3−1′	40	229·2	−0·56	1−3′	49
			1−4′	25			4−1′	25
	223·9	−1·69	4−1′	26	216·5	−0·18	1−4′	45
			1−3′	24			3−1′	17
			1−4′	22				
IIc	387·4	−0·55	1−1′	98	290·3	−0·59	1−2′	98
	261·2	−0·91	2−1′	88	237·4	−1·43	2−2′	86
	231·5	−1·35	1−3′	63	226·3	−2·03	3−1′	43
	217·6	−0·59	1−4′	50	213·6	−0·06	4−1′	55
IVa^b	385·7	−1·12	1−1′	98	289·3	−0·99	1−2′	79
	257·3	−1·66	3−1′	75	253·3	−0·25	2−1′	55
	229·7	−0·39	4−1′	55	227·6	−1·42	2−2′	69
	221·7	−1·35	1−3′	86	221·1	−2·22	1−4′	93
	201·7	−1·41	3−2′	63				
IVb^b	376·5	−0·91	1−1′	96	282·2	−0·90	1−2′	85
	259·6	−0·81	2−1′	73	251·4	−0·82	3−1′	53
	229·1	−0·12	4−1′	54	226·5	−1·47	2−2′	63
	221·8	−1·85	1−3′	83	204·5	−1·82	3−2′	58
IVc^b	368·2	−0·78	1−1′	98	276·5	−0·77	1−2′	96
	261·8	−2·07	2−1′	89	249·9	−1·38	3−1′	67
	243·1	−1·23	1−3′	62	225·6	−1·80	2−2′	60
	218·1	−0·21	4−1′	55	197·9	−1·37 •	3−2′	78

^{a} The dominant transition from the i-th occupied MO to the j-th unoccupied MO and its weight;
^{b} practically the same values ($\pm 3\%$) were calculated for the compounds III and IV.

of compounds *IV* and *VIII* in crystalline state[25-27] showed that their ester groups assume *syn-anti* conformation (which is approximately represented by structure *IV*). The calculations given in Table III show that the electronic absorption spectra of compounds *II—IV* can be interpreted only semiquantitatively by the PPP models of the structures *a—c*. The calculated position of the longest-wave band is not much remote from the experimental value in all the cases. The long-wave spectral region is best represented by the SCF models *IIa, IIIc, IVc*, whereas the short-wave region is best represented by the SCF models *IIb, IIIb, IVb*. This fact is connected obviously with non-planarity of the molecules *II—IV* under the conditions of the measurement and with limitation of π approximation of the calculations.
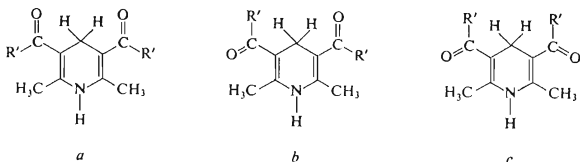
II, R′ = CH₃;   *III,* R′ = OCH₃;   *IV,* R′ = OC₂H₅

4-Phenyl derivatives V—VIII: The spectra of the 4-phenyl derivatives *V—VIII* show (in contrast to the 4-substituted 1,4-dihydropyridines *I—IV*) a shift of the long-wave maximum to shorter wave lengths, and they have two maxima in short--wave region. Crystallographic measurements[26,27] of compound *VIII* showed that the plane of phenyl group is practically perpendicular to that of double bonds of dihydropyridine nucleus. Therefrom it can be concluded that there is no important π interaction between the 4-substituent and 1,4-dihydropyridine nucleus. Therefore, we tried to calculate theoretical spectra of compounds *V—VIII* as superposition of spectra of two independent chromophores, *i.e.* the 4-unsubstituted compounds *I—IV* and toluene. Figure 1 compares the measured and the calculated spectral characteristics. Obviously the 4-substituent has minimum contribution to the long--wave spectral region in accordance with the original presumption.

4-o-Nitrophenyl derivatives IX—XII: We used an analogous simplification, *i.e.* interpretation of spectra of *IX—XII* as systems of two non-interacting chromophores — compounds *I—IV* and *o*-nitrotoluene. Besides the spectra of pure compounds *IX—XII* we also measured those of mixtures of equimolecular amounts of compounds *I—IV* and *o*-nitrotoluene. From Fig. 1 it follows that spectra of these mixtures resemble those of 4-unsubstituted derivatives in the long-wave region, which agrees with the presumptions. Comparison of the calculated electronic spectra of compound *I* and *o*-nitrotoluene with the experimental spectrum of their equimolecular

mixture shows a good agreement in position of maxima and intensities of transitions. Noteworthy is the middle band corresponding to $1-2'$ transition which is not present in the spectrum of compound I, in spectrum of compound IX being only indicated as an inflection. The interpretation of spectrum of compound IX by the
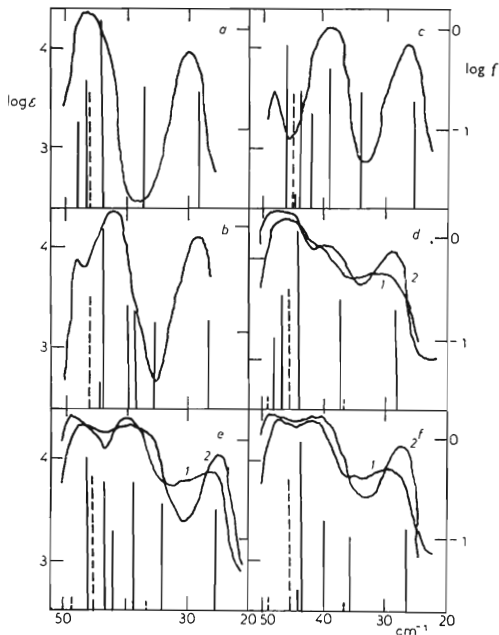

Fig. 1

Comparison of the experimental and the calculated electronic spectra. Spectrum a compound V; spectrum b compound VI; spectrum c compound $VIII$; spectrum d compound IX (curve 1), mixture of I and o-nitrotoluene (curve 2); spectrum e compound X (curve 1), mixture of compound II and o-nitrotoluene (curve 2); spectrum f compound XII (curve 1), mixture of compound IV and o-nitrotoluene (curve 2); spectra a and d model I; spectra b and e model IIb; spectra c and f model IVb; spectra a, b and c toluene (dashed line); spectra d, e and f o-nitrotoluene (dashed line)

calculations carried out for compound *I* and *o*-nitrotoluene is better in short-wave region, whereas the theoretical maxima have much too long wave lengths. Comparison of the calculated spectra of compound *IIb* and *o*-nitrotoluene with experimental spectrum of equimolecular mixture of compound *II* and *o*-nitrotoluene reveals a fairly good prediction of all four absorption bands (Fig. 1). No experimental maxima, however, were found which would correspond to the calculated electronic transitions in the region between the shortest-wave band and the next band. The spectrum of compound *X* can be interpreted similarly with the only difference that the calculated position of the second band has much too short wave length as it had in the spectra of diesters *XI* and *XII*. The spectra of mixtures of compounds *III* and *IV* with *o*-nitrotoluene show two main bands, the short-wave one being a superposition of three bands. Again the long-wave band corresponds to the transition $1-1'$ calculated for the substructures *IIIb* and *IVb*. The absorption bands in short-wave region can be assigned the corresponding electronic transitions calculated for both compounds *IIIb* or *IVb* and *o*-nitrotoluene. Again only the absorption maximum corresponding to the transition $1-2'$ predicted by the calculation is shifted to longer wave lengths as compared with experiment. The spectra of compounds *XI* and *XII* show four maxima, too. The longest-wave band is shifted considerably to higher wave lengths by the calculation, the other three maxima can be interpreted by means of the electronic transitions calculated for the substructures *IIIb*, *IVb*, and *o*-nitrotoluene inclusive of the transition $1-2'$.

The given results show that the semiempirical SCF PPP method can be used for interpretation of some typical features of electronic absorption spectra of relatively complex dihydropyridine derivatives *I—IV*. However, approximative character of the PPP method allows no unambiguous estimation of influence of real conformations of the studied compounds on their spectral characteristics.

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