ON DIHYDROPYRIDINES. XXVIII.*

A PPP STUDY OF THE ELECTRONIC SPECTRA OF 3,5-DICYANODIHYDROPYRIDINES AND CORRESPONDING ENAMINONITRILES

J. KUTHAN, V. SKÁLA and L. MUSIL

Department of Organic Chemistry,
Institute of Chemical Technology, 166 28 Prague 6

Received July 19th, 1972

The electronic absorption spectra of isomeric 3,5-dicyanodihydropyridines *I* and *II* and of similar enaminonitriles *III*—*V* were studied by means of Pariser–Parr–Pople (PPP method). All the maxima of the extinction curves in the near ultraviolet region were assigned to one-electron $\pi-\pi^*$ singlet-singlet transitions of corresponding chromophors. Problems of parametrization of corresponding quantum chemical models and the changes of π-electron distribution during excitation are discussed.

Although the ultraviolet spectra of dihydropyridine derivatives are often used for identification purposes, only limited information is available as to theoretical interpretation of spectral characteristics[1]. The calculations of Hantzsch 1,4-dihydropyridines and their 1,2-dihydro isomers by means of simple HMO method indicate a certain relation between the long-wavelength absorption band maximum and the calculated $N \rightarrow V_1$ transition energy[2,3]. The application of the more perfect PPP procedure resulted in good agreement with the positions and intensities of the absorption bands in the spectra of simple dihydropyridines[4,5]; worse results have been obtained, however, with structurally more complex dihydronicotinamides. The reason of these discrepancies is according to Evleth[4] the neglection of poly-excited configurations. A better agreement with experiment can be however achieved also by the use of more complicated parametrization considering also nonconjugated portions of the molecule.[6]

In the present work we centered on the use of standard PPP procedure to a study of isomeric 3,5-dicyanodihydropyridines *I* and *II*, whose chromophors are minimally influenced by steric effect of substituents[7-10], and of enaminonitriles *III*—*V* containing partial chromophoric fragment of compounds *I* and *II*.

---

* Part XXVII: This Journal *37*, 2764 (1972).

EXPERIMENTAL AND CALCULATIONS

The ultraviolet spectra of ethanolic solutions (c. $4 \cdot 10^{-5}$M) of the compounds were recorded on Optica Milano NI 4CF instrument. Substance *III* was prepared by borohydride reduction of malonitrile[11], compounds *I*, *II*, *IV*, and *V* were synthesized using reported procedures[7–9,12]. The spectra were measured with freshly distilled samples of enaminonitriles *III* and *IV*. Spectral characteristics used are recorded in Table I.

In calculations, the original PPP procedure[15–17] was adopted, with the use of sixteen monoexcited configurations and approximation of bicentric repulsion integrals according to Mataga and Nishimoto[18]. The calculation were carried out on Elliot 503 digital computer, using the standard program designed by Dr J. Pancíř, (J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague). Parameters used are listed in Table II. On variation of α and β "core" integrals, the following relations were used:

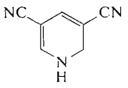
$$\begin{aligned}
\alpha^{c}_{\mu} &= \alpha^{0}_{\mu}[1 + 0{\cdot}4(q_{\mu} - Q_{\mu})]\,,\\
\beta^{c}_{\mu\nu} &= \beta^{0}_{\mu\nu}\exp(2{\cdot}597 - 1{\cdot}862 r_{\mu\nu})\,,\\
r_{\mu\nu} &= (1{\cdot}517 - 0{\cdot}18 p_{\mu\nu})\sqrt{6{\cdot}5/(Z_{\mu} + Z_{\nu})}\,,
\end{aligned}$$

where q_{μ} is the electron density at center μ in preceding iteration, Q_{μ} is "core" charge, $r_{\mu\nu}$ is the distance between centers μ and ν, $p_{\mu\nu}$ is the bond order in preceding iteration, and Z_{μ} and Z_{ν} are Slater exponents.

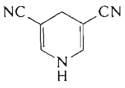
RESULTS AND DISCUSSION

The Spectra of Enaminonitriles III – V

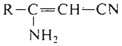
Aliphatic enaminonitriles *III* and *IV* exhibit in the near ultraviolet region only one-band spectra; with aromatic derivative *V*, an additional band, shifted to shorter wavelength occurs in the region of benzene chromophor (Table I). The results of PPP calculations for longest-wavelength absorption bands of substances *III* – *V* are presented in Table III. It is evident that the application of LCI procedure[16,17] leads to finding that they correspond to practically pure $N \rightarrow V_1$ transition between frontier MO's, *i.e.* to 96·5 – 98·2 per cent $1 \rightarrow 1'$. In addition, there exists a good agreement with geometry of the compounds investigated, the deviation of the theoretical from experimental spectral characteristics being always somewhat smaller for configurations prevailing in the sample measured. According to PMR spectra[21,22] and dipole moments[23], the mixture of *IIIa*, *IIIb* used in measurements contained 60% of Z-isomer *IIIb*, the *IVa,b* mixture approximately the same amount of *E*-isomer *IVa*, and the sample of substance *V* consisted exclusively of *E*-isomer *Va*. A certain bathochromic shift of experimental values of $\tilde{\nu}_{\max}$, relative to theoretical data, observed with substance *V* may be explained, in harmony with previous presumptions[24], by deviations from coplanarity of the molecules, due to interaction of *ortho* hydrogen atoms of the aromatic ring with the side chain. From the above facts we concluded



I

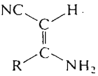


II

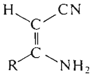


$R-\underset{NH_2}{\underset{|}{C}}=CH-CN$

III, R=H
IV, $R=CH_3$
V, $R=C_6H_5$



IIIa – Va



IIIb – Vb

as to the adequacy of "classical" parametrization[19] for the atoms and bonds of enaminonitrile chromophors. For that reason we did not use variation of α and β integrals. Especially the satisfactory application of hyperconjugation model of the methyl group[20] within the framework of SCF calculation of substance *IV* indicates significant π-overlap between this substituent and the rest of the molecule, which was already presumed in simple HMO calculation and has recently been supported by EHT study[22].

The Spectra of 3,5-*Dicyanodihydropyridines* I *and* II

The ultraviolet spectrum of 1,2-dihydro derivative *I* is typically three-band one[9], while in the spectra of 1,4-dihydro derivatives of type *II*, the much less intense second band can sometimes be observed only as a very weak inflex on the intense third

TABLE I
Spectral Characteristics of Compounds Investigated

Compound	$\tilde{\nu}_{max} \cdot 10^{-3}$, cm^{-1}	log ε	Source
3,5-Dicyano-1,4-dihydropyridine (*II*)	28·48	3·81	ref.[9]
	(42·5)[a]	(3·0)[a]	
	48·78	4·18	
3,5-Dicyano-1,2-dihydropyridine (*I*)	26·18	3·65	ref.[9]
	39·22	3·88	
	46·95	4·27	
3-Aminoacrylonitrile (*III*)	38·61	4·14	this work
3-Aminocrotonitrile (*IV*)	38·76	4·24	this work
3-Amino-3-phenylacrylonitrile (*V*)	34·13	4·00	ref.[12]
	44·25	4·04	

[a] Data for a weak shoulder; [b] literature data[13,14]: $\tilde{\nu}_{max}$ 38·760–39·060 cm^{-1}, log ε 4·13–4·27.

TABLE II

Standard Parametrization Used in SCF-MO-LCAO Calculations[a]

Atom	I, eV	A, eV	Ref.	Bond	E[b]	Ref.
$C(sp)^2$	11·16	0·03	18	$C(sp^2)$—$C(sp)$	0·9	—
$C(sp)$	11·19	0·10	18	$C(sp^2)$—$N(sp^2)$	0·8	20
$N(sp^2)$	27·50	9·20	19	$C(sp)$—$N(sp)$	1·4	27
$N(sp)$	14·18	1·66	18	$C(sp^2)$—CH_3	0·51	20
$C(H_3)$	11·42	0·58	19	$C(sp^2)$—CH_2	0·40	—
$C(H_2)$	11·42	0·58	—	$C{=}H_2$, $C{\equiv}H_3$	1·25	20
$H_3(C)$, $H_2(C)$	9·50	0·00	19	N—CH_2	0·32	—

[a] Ideal bond lengths (1·4 Å) and angles (120°) were adopted, except the following bonds: $C(sp^2)$—$C(sp)$ 1·46 Å, $C(sp)$—$N(sp)$ 1·16 Å, $C{=}H_2$ resp. $C{\equiv}H_3$ 1·1 Å; [b] in β-units ($\beta = -2{\cdot}388$ eV).

TABLE III

Calculated Characteristics of Long-Wavelength Absorption Bands of Enaminonitriles *III*—*V*

Nitrile (configuration)	$\tilde{\nu}_{max} \cdot 10^{-3}$, cm^{-1}	Δ^a	log ε^b	Δ^a	1 → 1′ %
IIIa (E)	39·76	+1·15	4·31	+0·17	97·6
IIIb (Z)	38·33	−0·28	4·12	−0·02	96·5
IVa (E)	37·99	−0·77	4·26	+0·02	98·2
IVb (Z)	37·03	−1·73	4·18	−0·06	96·9
Va (E)	32·35	−1·78	4·12	+0·12	97·8
Vb (Z)	30·46	−3·67	4·36	+0·36	97·6

[a] Deviation from experimental value (Table I); [b] calculated from oscillator strength f according to empirical formula $\log \varepsilon = \log f + 4{\cdot}4$.

band (Fig. 1 in ref.[8]). In harmony with these facts, all the PPP calculations performed during the present study showed that in the region followed ($25 . 10^3$ to $50 . 10^3$ cm^{-1}) both isomers *I* and *II* should exhibit at least three absorption bands. We used two approaches. First, the effect of the methylene group in position 2 or 4 was neglected or implicitly expressed by decreasing the values of the ionization potentials and electron affinities of the atoms bonded to the mentioned group (model A, inductive). Second, the methylene bridge was considered as a part of the π-electron system (model B, hyperconjugative). As follows from Table IV, the application of model A leads to more satisfactory positions of theoretical absorption bands with respect to the experimental ones (Table I) on using smaller empirical parameters of atoms bonded to the CH_2 group, *i.e.* in purely inductive approximation. Despite of this, in the case of 1,2-dihydro derivative the calculated maximum of the first absorption band is too shortwave, even though unequivalency of the polarity of the N—CH_2 and C—CH_2 bonds is considered. The introduction of variation of α core integrals improves somewhat the position of both calculated maxima, the variation of β core integrals has quite negative consequences in relation to experimental spectral characteristics. PPP data calculated with the use of model B (Table V) lead, similarly as in the cited work[6], to somewhat better characteristics of the long-wavelength maximum; the worse agreement with experiment is however obtained for the shorter wave-

TABLE IV

Calculated Characteristics of the Two Longest-Wavelength Absorption Bands in the UV Spectra of 3,5-Dicyanopyridines *I* and *II* (Model A[a])

1,2-Dihydro derivative *I*		1,4-Dihydro derivative *II*		Variable parameters[b]			
$\tilde{\nu}_{max} \cdot 10^{-3}$, cm^{-1}	log *f*	$\tilde{\nu}_{max} \cdot 10^{-3}$, cm^{-1}	log *f*	I_C, eV	A_C, eV	I_N, eV	A_N, eV
30·26	−0·27	30·72	−0·47	—	—	—	—
39·08	−0·47	40·25	−0·80				
31·08	−0·30	30·57	−0·48	dtto, α core variation			
40·70	−0·47	41·00	−0·89				
32·71	−0·57	34·51	−0·78	dtto, β core variation			
45·82	−1·14	43·42	−0·78				
32·98	−0·57	34·28	−0·78	dtto, α and β core variation			
46·05	−1·23	42·78	−0·81				
30·45	−0·33	31·27	−0·39	—	—	25·00^c	10·00^c
39·50	−0·47	40·61	−0·76				
29·70	−0·27	29·40	−0·37	10·4^d	−0·50^d	26·7^d	8·7^d
37·90	−0·45	39·65	−0·71				
29·94	−0·27	29·78	−0·37	10·7^d	−0·25^d	27·0^d	8·95^d
38·44	−0·46	40·20	−0·77				
30·63	−0·30	29·25	−0·37	dtto, α core variation			
39·87	−0·48	40·97	−0·87				
28·42	−0·30	—	—	dtto^e,	23·0^d	8·0^d	
39·87	−0·48						
29·03	−0·34	—	—	dtto^e, α core variation			
38·44	−0·37						

---

[a] In quantum chemical models the π-overlap with the methylene group was neglected; [b] only for atomic centers 1, 3, and 5, the others see Table II; [c] according to Evleth[5]; [d] only for the atoms bonded to the methylene group; [e] in the SCF model of substance *I* the unequivalency of C—CH_2 and N—CH_2 bonds was further considered the modification of values of I_N and A_N.

length maxima,* particularly of 1,4-dihydro isomer *II*, where the second calculated band is furthermore too intense and does not comport with the fact[25] that in the region around $38{\cdot}5 \,.\, 10^3$ cm^{-1} there is strong absorption maximum. By contrast, the effect of variation of core integrals and unequivalency of the NH—CH$_2$ and C—CH$_2$ bond are analogous to the model A.

TABLE V

Calculated Characteristics of Two Longest-Wavelength Absorption Bands in the UV Spectra of 3,5-Dicyanodihydropyridines *I* and *II* (Model B[a])

1,2-Dihydro derivative *I*		1,4-Dihydro derivative *II*		Variable parametrization[b]
$\tilde{\nu}_{max} . 10^{-3}$,cm^{-1}	log *f*	$\tilde{\nu}_{max} . 10^{-3}$,cm^{-1}	log *f*	
28·73	−0·40	28·86	−0·62	
37·53	−0·42	38·33	−0·60	
29·09	−0·43	28·20	−0·65	α core variation
38·87	−0·44	38·86	−0·62	
32·71	−0·54	32·42	−0·72	β core variation
45·05	−1·19	41·91	−0·79	
33·04	−0·53	33·81	−0·82	α and β core variation
45·13	−1·41	42·29	−0·74	
29·74	−0·32	30·21	−0·53	$k_{NH-CH_2} = 0{\cdot}16$,
38·26	−0·58	39·70	−0·71	$k_{C-CH_2} = 0{\cdot}2$
26·18	−0·52	—	—	$k_{NH-CH=} = 1{\cdot}0$, $k_{NH-CH_2} = 0{\cdot}8^c$
36·52	−0·27			
27·08	−0·56	—	—	dtto[c], α core variation
37·31	−0·26			

[a] In the SCF model the π-overlap with the methylene group was explicitly considered; [b] only changes with respect to the standard parametrization (Table II); [c] the parameters stress the unequivalency of the bonds in the $=$CH—NH—CH$_2$ grouping of substance *I*.

In Table VI are confronted the "best" calculated spectra with experimental data. It becomes immediately clear that, irrespective of the model used, all the maxima or inflexes observed on envelope extinction curves of substances *I* and *II* (Fig. 1) correspond to the bands with analogous one-electron dominant transitions between the couple of frontier bonding π-MO's (1 and 2) and antibonding π^*-MO's (1′ and 2′).

---

* The shift of the calculated $\tilde{\nu}_{max}$ towards higher values on going from model B to model A corresponds, in physical meaning, to the lowering of the hyperconjugative effect with decreasing number of hydrogen atoms on tetrahedral carbon centres of substances *I* and *II*. This effect may be in fact observed in the UV spectra of some 3,5-dicyanodihydropyridines (*cf.* refs[7–9,26]).

Especially the long-wavelength bands are from the point of view of configuration interaction practically pure N → V_1 transitions, *i.e.* 96·6–98·2% 1→1′. By this, the ultraviolet spectra of heteroolefinic substances *I* and *II* substantially differ from the spectrum of a similar, but heteroaromatic 3,5-dicyanopyridine (*cf.* ref.[27]).

Our PPP calculations of substances *I* and *II* obtained with the use of monoexcited configurations (Table V) do not yield worse relations with experimental characteristics of the spectra than the above mentioned studies of Evleth[4,5], considering for some simpler substances also bi-excited electron configurations, and especially for the model B they are similar to the data reported by Maggiore, Johansen and Ingraham[6]. We therefore presume that the attainment of the optimum agreement with experiment in the series studied is rather the problem of complicated parametrization of dihydropyridine compound in PPP method, which is associated with simultaneous operation of the inductive and hyperconjugative effects of tetrahedral carbon centres of the heterocyclic system.

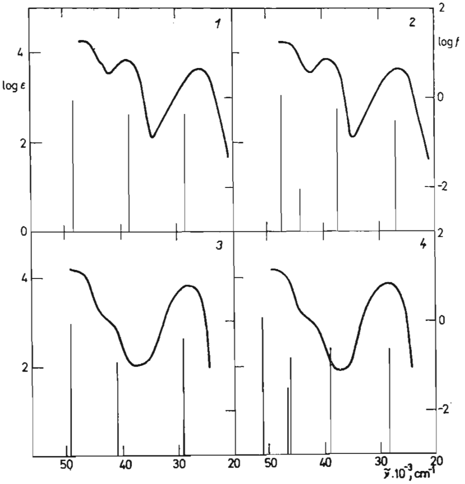


FIG. 1

Comparison of the Experimental with Calculated Electronic Spectra

Spectra *1* and *2* 3,5-dicyano-1,2-dihydropyridine (*I*); spectra *3* and *4* 3,5-dicyano-1,4-dihydropyridine (*II*); spectra *1* and *3* inductive model A and spectra *2* and *4* hyperconjugative model B.

π-Electron Distribution in the Ground and Excited States

The calculated π-electron distribution and its changes during electronic excitation are in the case of the compounds studied little dependent on the model chosen. For that reason discussion will be restricted only to the results obtained by means of inductive approximation (model A for substance *I* and *II*). In Figs 2 and 3 are shown the SCF molecular diagrams of the ground state of substances *I*–*III*, which illustrate a minimum effect of *cis–trans* isomerism on enaminonitriles *III* – *V* and a similarity with the π-electron density calculated earlier 2,24 for substances *I* – *V* by simple HMO method. Typical difference of the SCF π-electron distribution is the higher bond order of the bonds of the amino group and of the heterocyclic nitrogen atom, with the adjacent carbon atom, the higher density at the last mentioned atom, and the reduced conjugation of the nitrile groups with the residual unsaturated system of the molecules.

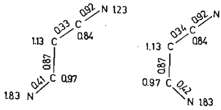


FIG. 2

SCF Molecular Diagrams of Z- and E-Isomers of 3-Aminoacrylonitrile (*III*)

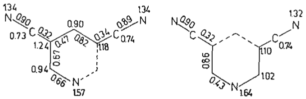


FIG. 3

SCF Molecular Diagrams of 3,5-Dicyanodihydropyridines *I* and *II* (Inductive Model A)

In Tables VII and VIII are summarized the changes in π-electron densities Δq and π-bond orders Δp induced by dominant singlet-singlet transitions $1 \rightarrow 1'$ and $2 \rightarrow 1'$ in the first two absorption bands of substances *I*–*III*. In all the cases the above excitations bring about the shift of π-electrons towards the nitrile groups. Thus, for example, both one-electron transitions mentioned increase π-electron density at the nitrile group in the expense of the other atom centers in 1,2-dihydro derivative *I* by 0·322 and 0·034 electron, respectively, and in 1,4-dihydro isomer *II* by 0·154 and 0·138 electron, respectively. The changes in π-electron distribution during the $1 \rightarrow 1'$ excitation of substance *III* are of similar features as in the case of dihydro derivatives *I* and *II*. As follows from Table VII, the densities q are increased in the main in positions 1' and 3 and, further, the differences in bond order p are smooth out in the sense of formula *VI*. An analogous type of π-electron shifts then corresponds to the domi-

TABLE VI

Comparison of Best PPP Calculations on 3,5-Dihydropyridines *I* and *II* with Experimental Data

Substance (Model[a])	$\tilde{\nu}_{max} \cdot 10^{-3}$, cm^{-1}	Δ^b	$\log \varepsilon^c$	Δ^b	$i \to j$ %[d]
I(A)	29·03	+2·85	3·86	+0·21	1 → 1′ 97·6
	38·44	−0·78	3·83	−0·05	1 → 2′ 90·1
	48·25	+1·30	4·18	−0·09	2 → 1′ 83·6
II (A)	29·25	+0·76	3·83	+0·02	1 → 1′ 98·8
	40·97	−1·53[e]	3·33	+0·3[e]	1 → 2′ 76·6
	49·28	+0·50	4·22	+0·04	2 → 1′ 66·2
I (B)	27·08	+0·90	3·64	−0·01	1 → 1′ 96·6
	37·31	−1·91	3·94	+0·06	1 → 2′ 88·8
	43·90	[f]	2·13	[f]	1 → 3′ 93·3
	47·57	+0·62	4·26	−0·01	2 → 1′ 69·6
II(B)	28·20	+0·29	3·55	−0·26	1 → 1′ 98·2
	38·86	−3·6[e]	3·58	+0·5[e]	1 → 2′ 83·1
	45·91	[f]	3·40	[f]	3 → 1′ 94·5
	46·68	[f]	2·72	[f]	1 → 3′ 88·3
	51·03	+2·25	4·31	+0·13	2 → 1′ 76·0

[a] Inductive A, hyperconjugative B (Tables IV and V); [b] deviation from experimental value; [c] calculated according to empirical formula $\log \varepsilon = \log f + 4{\cdot}2$; [d] dominant transition from *i*-th bonding MO to *j*-th antibonding MO and its weight; [e] comparison with inaccurate value for inflex (Table I); [f] no maximum on the envelope extinction curve corresponds to the band (Fig. 1).

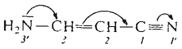
TABLE VII

Changes in π-Electron Distribution of Stereoisomeric 3-Aminoacrylonitriles (*IIIa,b*) Induced by the Transition from HOMO to LUMO (1→1′)

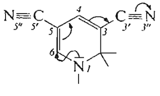
Position	Bond[a]	*E*-Isomer *IIIa*		*Z*-Isomer *IIIb*	
		Δ*q*	Δ*p*	Δ*q*	Δ*p*
1	1−1′	+0·24	−0·36	+0·20	−0·21
1′	1−2	+1·23	+0·15	+0·16	+0·17
2	2−3	−0·24	−0·37	−0·21	−0·42
3	3−3′	+0·26	+0·05	+0·27	+0·05
3′		−0·40	—	−0·38	—

[a] For designation of atomic centers see formula *VI*.

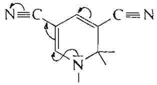
nant 2→1′ transition of the second absorption band of dihydro isomers *I* and *II* (Table VIII and formulae *VIIa* and *VIIIa*). A slightly different situation is observed



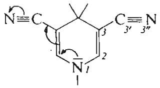
VI



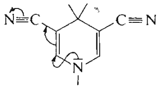
VIIa



VIIb



VIIIa



VIIIb

TABLE VIII

Changes in π-Electron Distribution of 3,5-Dicyanodihydropyridines *I* and *II* Induced by Dominant Transitions in the First Two Absorption Bands[a]

Substance	Position[b]	Electron densities[c]		Bond[b]	Bond orders[c]	
		$\Delta q_{(1\rightarrow 1')}$	$\Delta q_{(1\rightarrow 2')}$		$\Delta p_{(1\rightarrow 1')}$	$\Delta p_{(1\rightarrow 2')}$
I	1	−0·10	−0·15	3—3′	+0·08	−0·02
	3	−0·12	−0·26	3′—3″	−0·06	−0·04
	3′	+0·07	+0·05	3—4	−0·24	−0·17
	3″	+0·02	−0·02	4—5	+0·12	−0·04
	4	+0·22	+0·11	5—5′	−0·02	+0·13
	5	−0·27	−0·15	5′—5″	+0·01	−0·17
	5′	−0·001	+0·20	5—6	−0·17	−0·24
	5″	−0·06	+0·09	1—6	−0·10	−0·02
	6	+0·23	+0·14			
II	1	−0·27	−0·09	1—2	+0·11	−0·06
	2	+0·16	+0·14	2—3	−0·29	−0·27
	3	−0·10	−0·15	3—3′	+0·08	+0·06
	3′	+0·06	+0·06	3′—3″	−0·06	−0·06
	3″	+0·02	+0·01			

[a] Inductive model A (Table IV); [b] for designation of atomic centers see formulae *VIIa* and *VIIIa*; [c] subscripts denote electronic transitions (Table VI).

for the 1→1′ transition of 1,4-dihydro derivative *II*, where the bond order p between positions 1 and 2 (formula *VIIIb*) increases, whereas in 1,2-dihydro derivative *I* π-electrons are shifted from the heterocyclic nitrogen towards the nitrile group in position 3 (formula *VIIa*). Similar changes in the course of the excitation have been already stated[6] also in the case of isomeric dihydronicotinamides.

The calculated π-component of the dipole moment of substance *II* is likely oriented as the σ-component (in the direction from position 1 towards position 4) and is for the ground state 5·6 D; it differs only slightly for both excited states (6·9 and 5·3 D). This is in harmony with low sensitivity of the ultraviolet spectra of 3,5-dicyano-1,4-dihydropyridines towards solvent effects[1,7,8]. Calculated vectors of the dipole moments of excited states of substances *I* and *III* are, in absolute values, as a rule higher than those of the ground states. They are, however, of different directions, so that their effect on the total dipole moment of molecules of these compound could not be reliably estimated. It is remarkable that π-electron shifts expressed according to the data listed in Tables VII and VIII by formulae *VI*, *VIIa,b*, and *VIIIa,b* are essentially in harmony with the canonical valence bond formulae considered earlier[28–30] in discussing qualitatively the ultraviolet spectra of some dihydropyridine derivatives.

The authors thank Dr E. Janečková of this Institute for UV spectra measurements.

REFERENCES

1. Eisner U., Kuthan J.: Chem. Rev. *72*, 1 (1972).
2. Kuthan J.: This Journal *32*, 1280 (1967).
3. Kuthan J., Paleček J.: This Journal *34*, 1339 (1969).
4. Evleth E. M.: J. Chem. Phys. *46*, 4151 (1967).
5. Evleth E. M.: J. Am. Chem. Soc. *89*, 6445 (1967).
6. Maggiora G., Johansen H., Ingraham L. L.: Arch. Biochem. Biophys. *131*, 352 (1969).
7. Hofmann D., Kosower E. M., Wallenfels K.: J. Am. Chem. Soc. *83*, 3314 (1961).
8. Kuthan J.: This Journal *27*, 2175 (1962).
9. Kuthan J., Janečková E.: This Journal *29*, 1654 (1964).
10. Brignell P. J., Eisner U., Farrell P. G.: J. Chem. Soc. (B) *1966*, 1083.
11. Sieveking H., Lüttke W.: Angew. Chem. *11*, 342 (1969).
12. Kuthan J., Hakr J.: This Journal *32*, 1438 (1967).
13. Conn J. J., Taurins A.: Can. J. Chem. *31*, 1211 (1953).
14. Kurtz P., Gold H., Disselnkötter H.: Ann. *624*, 1 (1959).
15. Pople J. A.: Trans. Faraday Soc. *49*, 1375 (1953).
16. Pariser R., Parr R. G.: J. Chem. Phys. *21*, 466 (1953).
17. Pariser R., Parr R. G.: J. Chem. Phys. *21*, 767 (1953).
18. Mataga N., Nishimoto K.: Z. Physik. Chem. (Frankfurt) *13*, 140 (1957).
19. Hinze J., Jaffé H. H.: J. Am. Chem. Soc. *84*, 540 (1962).
20. Pancíř J.: Private communication.
21. Bullock E., Gregory B.: Can. J. Chem. *43*, 332 (1965).
22. Kuthan J., Paleček J.: Unpublished results.

23. Kuthan J., Jehlička V., Hakr E.: This Journal *32*, 4309 (1967).
24. Kuthan J.: This Journal *34*, 2942 (1969).
25. Janečková E., Kuthan J.: This Journal *29*, 1495 (1964).
26. Kuthan J., Janečková E., Havel M.: This Journal *29*, 143 (1964).
27. Skála V., Kuthan J.: This Journal *35*, 2378 (1970).
28. Wallenfels K., Schüly H., Hofmann D.: Ann. *621*, 106 (1959).
29. Kuthan J.: *Thesis*. Institute of Chemical Technology, Prague 1960.
30. Hanstein W., Wallenfels K.: Tetrahedron *23*, 585 (1967).

Translated by J. Hetflejš.