

ELECTRONIC ABSORPTION SPECTRA AND π -ELECTRON STRUCTURE OF 2-PROPENYLIDENE-1,2-DIHYDROPYRIDINE AND ITS DERIVATIVES

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The results of the PPP calculations of the singlet-singlet transitions of 1-methyl-3'-cyano-3'-alkoxycarbonyl-2-propenylidene-1,2-dihydropyridines *II* and 1-methyl-4-amino-3,3'-dicyano-3',5'-di(methoxycarbonyl)-2-propenylidene-1,2-dihydropyridine (*III*) are in a satisfactory agreement with the experimental absorption curves in the visible and near ultraviolet region. Based on this finding, the absorption of the parent heterocyclic system of 2-propenylidene-1,2-dihydropyridine (*I*) is predicted. Some aspects of the π -electron structure of the substances *I*–*III* in the S_0 , S_1 , and S_2 states are discussed.

Although a series of 2-propenylidene-1,2-dihydropyridine (*I*) derivatives have been prepared^{1–11}, little is known about their optical properties and electronic structure. In the papers^{4–6}, only data on the positions of the long-wavelength absorption peaks in the region 345–475 nm can be found. Studying relations between the structure and optical properties, we have now dealt with the recently described^{8–11} functional derivatives 1-methyl-3'-cyano-3'-alkoxycarbonyl-2-propenylidene-1,2-dihydropyridines (*II*, $R^1 = \text{CH}_3$, $R^3 = \text{CO}_2\text{CH}_3$ or $\text{CO}_2\text{C}_2\text{H}_5$) and 1-methyl-4-amino-3,3'-dicyano-3',5'-di(methoxycarbonyl)-2-propenylidene-1,2-dihydropyridine (*III*, $R^1 = \text{CH}_3$, $R^2 = \text{CO}_2\text{CH}_3$), which can be isolated as stable substances in the crystalline state. We calculated their electronic absorption spectra by the standard PPP method and confronted the results with the experimental data. We paid particular attention also to the π -electron structure of the substances *I*–*III* in their ground and lowest excited states.

EXPERIMENTAL

The temperature data have not been corrected. The melting points were determined on a Boetius stage. The spectral characteristics were measured by employing instruments Specord UV VIS (Zeiss, Jena), Varian XL-100, Perkin-Elmer 625, and LKB 9000.

1-Methyl-3'-cyano-3'-methoxycarbonyl-2-propenylidene-1,2-dihydropyridine (*II*, $R^3 = \text{CO}_2\text{CH}_3$). The substance was prepared analogously as the 3'-ethoxycarbonyl derivative *II* (see below) by reaction of 1,2-dimethylpyridinium iodide with methyl methoxymethylenecyanoacetate

in the presence of potassium carbonate, and chromatographic separation of the reaction mixture. Yield 70% fine orange crystals, m.p. 174–175°C, whose MS exhibits the molecular peak m/e 216, in accordance with the formula $C_{12}H_{12}N_2O_2$. VIS-UV spectrum (ethanol): $\tilde{\nu}_{\max}$ 22.1 kcm^{-1} ($\log \epsilon$ 4.65), inflexion at 26.0 kcm^{-1} , and $\tilde{\nu}_{\max}$ 43.0 kcm^{-1} ($\log \epsilon$ 3.97); see Fig. 1. IR spectrum (chloroform): 1240 cm^{-1} $\nu(\text{C}=\text{O})$, 1530, 1578, 1637, and 1679 cm^{-1} $\nu(\text{conj. C}=\text{C}$ and $\text{C}=\text{O})$, 2201 cm^{-1} $\nu(\text{conj. C}\equiv\text{N})$. $^1\text{H-NMR}$ spectrum (deuteriochloroform): δ 3.62 s (CH_3N), δ 3.76 s (CH_3O), δ 5.52 d and δ 8.16 d, $^3J_{\text{HH}} = 14$ Hz ($\text{trans}=\text{CH}-\text{CH}=\text{}$), δ 6.4 t ($\text{C}(5)-\text{H}$), δ 7.1–7.6 m ($\text{C}(3)-\text{H}$, $\text{C}(4)-\text{H}$, and $\text{C}(6)-\text{H}$).

1-Methyl-3'-cyano-3'-ethoxycarbonyl-2-propenylidene-1,2-dihydropyridine (II, $\text{R}^3 = \text{CO}_2\text{C}_2\text{H}_5$) This substance was prepared according to the paper⁹ in a 45% yield. M.p. 142–145°C, ref.⁹ 143–146°C. The UV-VIS and IR characteristics are analogous as for the above described 3'-methoxycarbonyl derivative II. $^1\text{H-NMR}$ spectrum (deuteriochloroform): δ 1.32 t and 4.22 q, $^3J_{\text{HH}} = 7$ Hz ($\text{C}_2\text{H}_5\text{O}$), δ 3.64 s (CH_3N), δ 5.52 d and 8.17 d, $^3J_{\text{HH}} = 14$ Hz ($\text{trans}=\text{CH}-\text{CH}=\text{}$), δ 6.40 t ($\text{C}(5)-\text{H}$), δ 7.1–7.6 m ($\text{C}(3)-\text{H}$, $\text{C}(4)-\text{H}$, and $\text{C}(6)-\text{H}$). Analogous characteristics were measured for solution in DMSO- d_6 : 2.14 t and 4.00 q, 3.65 s, 5.19 d and 7.96 d, 6.64 td, and 7.3–7.9 m. With this solution, NOE experiments were performed in the same conditions as in the work¹¹.

1-Methyl-4-amino-3,3'-dicyano-3',5'-di(methoxycarbonyl)-2-propenylidene-1,2-dihydropyridine (III). The preparation of this compound has been described previously¹¹, m.p. 302–304°C. UV-VIS spectrum (ethanol): $\tilde{\nu}_{\max}$ 20.6 kcm^{-1} ($\log \epsilon$ 4.93), shoulder 25.0 kcm^{-1} , $\tilde{\nu}_{\max}$ 33.2, 37.5, 40.2, and 46.3 kcm^{-1} ($\log \epsilon$ 3.55, 4.20, 4.32, and 4.30, respectively) and shoulder at 44.8 kcm^{-1} . IR spectrum (KBr disc): 1640 and 1690 cm^{-1} $\nu(\text{conj. C}=\text{C}$ and $\text{C}=\text{O})$, 2200 cm^{-1} $\nu(\text{C}\equiv\text{N})$, 3165 and 3320 cm^{-1} $\nu(\text{N}-\text{H}\cdots\text{O})$. $^1\text{H-NMR}$ spectrum (DMSO- d_6): δ 3.57 s (CH_3N), δ 3.70 s and 3.82s (two nonequivalent CH_3O), δ 5.74 d and 8.82 d, $^3J_{\text{HH}} = 14$ Hz ($\text{trans}=\text{CH}-\text{CH}=\text{}$), δ 8.12 s ($\text{C}(6)-\text{H}$), and δ 9.12 broad (NH_2).

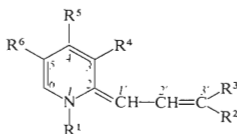
CALCULATIONS

The SCF models of the substances studied were calculated in the PPP version^{12–14} on a computer Elliot 503. The \mathbf{F} matrix elements were expressed according to Pople¹² and the monocentric Coulomb integrals were approximated by the ionization potentials, which were taken from the paper¹⁵ together with the electron affinities. The resonance integrals were expressed in the β units ($\beta = -2.388$ eV). The hyperconjugation model was adopted for the methyl group CH_3-N immediately bonded to the π -electron system of the heterocycle, the heteroatomic model was applied to the ester CH_3O group. The heterocyclic part of the molecules of the substances II and III was approximated by a geometrically regular hexagon with the bond angles 120°, the same angles were used for the other sp^2 atomic centres, whereas for the $\text{C}-\text{CN}$ and $\text{X}-\text{CH}_3$ groupings, their linearity was respected. The other parameters of the calculations are given in Table I. The bicentric repulsion integrals were calculated according to Mataga and Nishimoto¹⁴. The extent of the LCI was confined to 25 monoexcited configurations ψ_{i-j} pertaining to the electron transitions from the i -th to the j -th MO's.

RESULTS AND DISCUSSION

The parent heterocycle I is conceivable in two stereoisomeric forms *E* (formula Ia) and *Z* (formula Ib). The hitherto prepared derivatives II and III exist, however, exclusively in the configuration *E*, as indicated by the positive NOE effect observed

in the $^1\text{H-NMR}$ spectra of selected derivatives on the signals for the positions 1' and 6 after irradiation of the signal $\text{R}^1 = \text{CH}_3$ (ref.¹¹ and Experimental). On the other hand, the configurations of the substituents R^2 and R^3 at the end of the side chain as well as the conformations of the ester groups R^3 or R^3 and R^6 have not been elucidated. With regard to this, we confined the selection of the PPP models of the substances *II* and *III* to the structures *IIa* and *IIIa-c* ($\text{R} = \text{CH}_3$) hoping that they may correspond to or approach the actual geometry of the examined molecules in the conditions of the spectral measurements. The analogous PPP calculations for the stereoisomers *Ia* and *Ib* ($\text{R} = \text{CH}_3$) acquire then the character of prediction of so far unknown experimental data. For a confrontation of the results obtained with the experimental values, the spectral characteristics of the two substances of the type *II* ($\text{R}^1 = \text{CH}_3$ and $\text{R}^2 = \text{CH}_3$ or C_2H_5) and of one representative of the type *III* ($\text{R}^2 = \text{R}^6 = \text{CO}_2\text{CH}_3$) were chosen.



- I*, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{R}^6 = \text{H}$
II, $\text{R}^1 = \text{alkyl}$, $\text{R}^2 = \text{CN}$, $\text{R}^3 = \text{COO alkyl}$, $\text{R}^4 = \text{R}^5 = \text{R}^6 = \text{H}$
III, $\text{R}^1 = \text{alkyl}$, $\text{R}^2 = \text{R}^4 = \text{CN}$, $\text{R}^3 = \text{R}^6 = \text{COO alkyl}$, $\text{R}^5 = \text{NH}_2$

TABLE I
Parameters of the SCF Calculations
 $h_x = 0$ was used for the zeroth iteration in all the SCF calculations.

Atom X	<i>I</i> eV	<i>A</i> eV	k_{CX}^a	<i>Z</i>	r_{CX}^a nm
$\text{C}(sp^2)$	11.6	0.03	1.0	1	0.139
$\text{C}(sp)$	11.19	0.10	0.9	1	0.146
$\text{C}(sp^3)$	11.42	0.58	0.51	1	0.152
$\text{N}(sp^2)$	14.12	1.78	1.0	1	0.139
$\text{N}(sp)$	14.18	1.66	1.4 ^b	1	0.114 ^b
$\text{H}_3\equiv\text{C}$	9.50	0.0	1.25 ^c	1	0.110 ^c
$\text{O}(\text{CH}_3)$	33.0	11.47	0.78	2	0.137
$\text{O}=\text{C}$	17.28	2.7	1.6	1	0.124

^a For $\text{C}(sp^2)$ unless stated otherwise; ^b for $\text{C}(sp)$; ^c for a formal π -bond $\text{C}\equiv\text{H}_3$.

Electronic spectra. The spectra of the ethanolic solutions of all the substances *II* and *III* examined display in the region $20\text{--}50\text{ cm}^{-1}$ the same characteristic features as to the absorption band maxima and intensities. In the visible region they exhibit an absorption maximum at 22.1 and 20.6 cm^{-1} , respectively, with a short-wavelength shoulder at 26.0 and 25.0 cm^{-1} , respectively. In the ultraviolet range, the chromophoric systems in question give rise to absorption maxima at 43.0 cm^{-1} and $32.2, 37.5, 40.2,$ and 46.3 cm^{-1} , respectively.

The spectral characteristics calculated for the various SCF models *Ia–IIIc* are given in Table II, in Figs 1 and 2 some of these theoretical data are confronted with the experimental absorption curves. Obviously our PPP calculations are able to account for the positions of virtually all the pronounced maxima, hence based on the $\pi \rightarrow \pi^*$ transitions. In the case of the mutually overlapping absorption bands in the visible spectral region, however, the calculated oscillator strengths are too low for the longer-wavelength bands and too high for the shorter-wavelength bands. Regarding the initial simplifying assumptions, such as the extent of the CI, the ideal geometry, the simple fixed parametrization, *etc.*, we are not able to offer an explanation of this discrepancy. Still, based on the generally satisfactory agreement between the theoretical and experimental spectra it can be taken for very likely that the intense long-wavelength absorption of the substances *II* and *III* really corresponds to the $S_0 \rightarrow S_1$

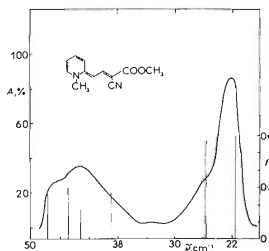


FIG. 1

Comparison of the Visible — Near Ultraviolet Absorption Curve of 1-Methyl-3'-cyano-3'-methoxycarbonyl-2-propenylidene-1,2-dihydropyridine (*II*) with the PPP Calculation for the SCF Model *IIa*

Solutions in ethanol, $c = 4 \cdot 10^{-6}$ mol/l, $d = 50$ mm; the verticals denote schematically the calculated absorption bands.

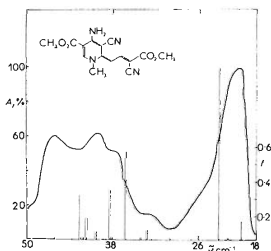


FIG. 2

Comparison of the Absorption Curve of 1-Methyl-4-amino-3,3'-dicyano-3',5'-di(methoxycarbonyl)-2-propenylidene-1,2-dihydropyridine (*III*) with the PPP Calculation for the SCF Model *IIIa*

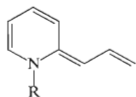
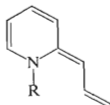
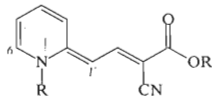
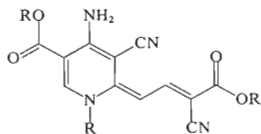
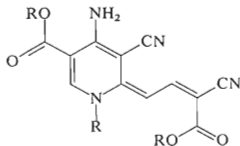
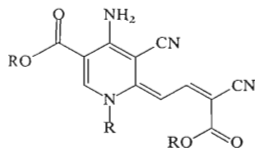
Solution in ethanol, $c = 4 \cdot 10^{-6}$ mol/l, $d = 50$ mm; only the 8 longest-wavelength theoretical absorption bands are denoted by verticals.

TABLE II
Spectral Characteristics of the Singlet-Singlet Transitions Calculated by the PPP Method

$E \cdot 10^{-3}$ cm^{-1}	$\log f$	$i-j^a$	W^b %	$E \cdot 10^{-3}$ cm^{-1}	$\log f$	$i-j^a$	W^b %
Model Ia				Model IIIa			
20.89	-0.705	1-1'	87	20.01	-0.997	1-1'	95
29.76	-0.075	1-2'	84	23.30	0.003	1-2'	92
36.37	-0.837	1-3'	94	33.37	-1.253	1-3'	56
41.07	-0.389	2-1'	60			2-1'	31
41.80	-1.489	1-4'	59	36.06	-0.296	2-2'	42
46.05	-0.642	3-1'	60			1-3'	29
50.01	-1.204	1-5'	71	38.20	-0.559	2-1'	37
51.89	-1.057	3-2'	43			1-4'	28
Model Ib				40.36	-1.315	1-4'	57
20.84	-0.803	1-1'	88	41.42	-0.924	1-5'	57
29.14	-0.097	1-2'	83	42.42	-0.602	3-1'	40
35.87	-0.876	1-3'	95			1-5'	33
41.02	-0.296	2-1'	44	Model IIIb			
41.68	-1.090	1-4'	51	19.08	-1.095	1-1'	97
		2-1'	31	23.62	0.038	1-2'	94
45.18	-0.606	3-1'	68	32.06	-0.766	2-1'	48
49.77	-1.059	1-5'	69			1-3'	37
51.74	-0.566	3-2'	46	35.56	-0.303	1-3'	49
Model IIa						2-2'	26
21.36	-0.218	1-1'	95	37.44	-0.836	1-4'	36
25.81	-0.240	1-2'	94			2-2'	30
38.84	-2.001	1-3'	63	39.32	-1.312	1-4'	52
		2-1'	25	41.46	-0.964	1-5'	74
39.11	-0.548	2-1'	59	41.89	-0.601	3-1'	55
		1-3'	27	Model IIIc			
40.16	-2.262	1-4'	75	19.83	-1.014	1-1'	95
43.24	-0.775	1-5'	65	23.71	0.055	1-2'	92
		3-1'	27	33.31	-1.388	1-3'	61
44.99	-0.527	3-1'	40			2-1'	28
		1-5'	27	35.94	-0.218	2-2'	36
47.89	-0.547	2-2'	38			1-3'	25
				38.16	-0.754	1-4'	31
						2-1'	30
				40.22	-1.275	1-4'	54
				41.43	-0.703	1-5'	68
				42.33	-0.654	3-1'	53

^a The most significant transitions from the i -th bonding MO to the j -th antibonding MO; ^b transition weight.

and $S_0 \rightarrow S_2$ excitations in the sense of the PPP calculations, each of them being due – according to the weights of the configuration $\psi_{1-1'}$ and $\psi_{1-2'}$ – to virtually a single $\pi \rightarrow \pi^*$ transition, $1 \rightarrow 1'$ or $1 \rightarrow 2'$ (Table II). The contribution of the higher monoexcited ψ_{1-j} configurations to these absorptions is negligible as compared with the excitation to the S_3 state and higher in the near ultraviolet region, where several $\pi \rightarrow \pi^*$ transitions participate appreciably in each of the absorption bands. It can be thus concluded that the colour behaviour of the substances *II* and *III* investigated is governed essentially by their S_1 and S_2 states whose energy is to a high degree affected by the HOMO and the two lowest unoccupied π^* -MO.

*Ia* (E)*Ib* (Z)*IIa**IIIa**IIIb**IIIc*

It is also apparent from Table II that for the parent chromophoric systems *Ia,b* a similar spectral behaviour can be predicted, with a $0.5-1.8 \text{ km}^{-1}$ blue shift of the long-wavelength absorption as compared with the substances *II* and *III*, and with a small effect of the configuration *E* or *Z*. Rather exceptional is here only the character of the third excitation $S_0 \rightarrow S_3$, exhibiting as the absolutely dominant the electron configuration $\psi_{1-3'}$. From a comparison of the calculated data for the

models *IIIa-c* it is also clear that geometrical details such as the configurations of the R^2 and R^3 groups at the centre $3'$ or the conformations of the R^2 and R^6 ester groups affect the spectral characteristics so little that use cannot be made of the PPP method for a study of these stereochemical aspects of the compounds *I-III*. We could generalize this statement based on the PPP calculations of twenty other derivatives containing the parent skeleton *I*, performed at our laboratory¹⁶; these calculations also indicated that substitution in the side chain affects the electronic absorption spectra usually more markedly than analogous substitution in the heterocyclic part of the molecule.

π -Electron structure. For the behaviour of the substances *I-III* in darkness and in the visible light, their π -electron structure in the S_0 , S_1 , and S_2 states is of importance.

The situation in the ground state S_0 approximated always by the configuration 1 shows that the positive π -charges in the skeleton *Ia* ($R = CH_3$) are localized exclusively in the positions 4 and $2'$ ($q_1 = 0.989$ and 0.997 , respectively), whereas at the other centres $-1, 2, 3, 5, 6, 1',$ and $3'$ — only negative π -charges are found ($q_1 = 1.594, 1.038, 1.016, 1.060, 1.028, 1.169,$ and 1.085 , respectively). The introduction of the substituents R^2 and R^3 in the derivative *II* brings about a characteristic decrease of the π -electron density in the position $2'$ (0.897) and increase in the posi-

TABLE III

Comparison of the Olefinic Proton Signals δ_i of the Substances *II* and *III* With the π -Electron Densities q_i at the Corresponding Carbon Centres i

Compound	Proton signal, δ_i		q_i^a	i
	in $CDCl_3$	in $DMSO-d_6$		
<i>II</i> , $R^1 = CH_3$, $R^3 = CO_2C_2H_5$	8.17	7.97 ^b	0.897	$2'$
			0.965	4
	7.1–7.6 ^c	7.2–7.9 ^{c,d}	1.009	3
			1.018	6
	6.40	6.65	1.044	5
	5.52	5.39 ^e	1.173	$1'$
<i>III</i> , $R^1 = CH_3$, $R^3 = R^6 = CO_2CH_3$	<i>f</i>	8.82	0.895	$2'$
	<i>f</i>	8.12	0.940	6
	<i>f</i>	5.74	1.173	$1'$

^a For the SCF models *IIa* and *IIIa*; ^b a 3% lowering of intensity found on irradiation of the R^1 group protons; ^c region of multiplets of higher order subspectrum; ^d the part of the spectrum at 7.9δ exhibits a 12% intensity increase on irradiation of the R^1 protons; ^e displays 30% NOE on irradiation of the R^1 group protons; ^f not measured because of the low solubility.

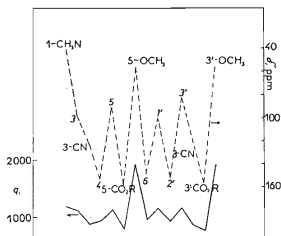
tions 1' and 3' (0.173 and 1.142, respectively). At the heterocyclic ring, the densities decrease analogously — by 0.007 to 0.037 — with no change of the charge sign. Additional substituents R^4 to R^6 in the substance *III* give rise to a positive π -charge in the position 6 and an additional increase of the π -electron densities in the positions 3 and 5 (1.140 and 1.125, respectively). That the SCF values of q_i of the model *IIIa* are physically reasonable is corroborated by their satisfactory conformity with the chemical shifts δ_i^C in the ^{13}C -NMR spectrum of the substance *III* ($R^1 = \text{CH}_3$, $R^3 = R^6 = \text{CO}_2\text{CH}_3$). It is apparent from Fig. 2 that the carbon atoms possessing lower q_i values exhibit systematically higher chemical shifts and *vice versa*. Table III demonstrates that the analogous effect of the π -electron densities q_i on the chemical shifts δ_i^H in the ^1H -NMR spectra of the substances *II* and *III* ($R^1 = \text{CH}_3$, $R^3 = R^6 = \text{CO}_2\text{CH}_3$ or $\text{CO}_2\text{C}_2\text{H}_5$) is appreciable, too. The triplet or the triplet of doublets at δ 6.4–6.6 in the spectrum of the substance *II* can be thus attributed to the proton in the position 5 with a high probability, regarding the relatively high π -electron density ($q_5 = 1.044$). Furthermore, the cause of the anomalously low δ_i^H values for the position 2' (5.39 and 5.52, respectively) can be sought in the high π -electron density, 1.173. The additional increase of this chemical shift for the compound *III* to the value $\delta_2^H = 5.74$ can be explained in terms of the paramagnetic anisotropic effect of the spatially nearby cyano group in the position 3, which becomes the secondary factor here.

The delocalization of the π -electrons in the chromophoric systems *I–III* is well described by the π -bond orders p_{ij} between the i -th and j -th atomic centres. From Fig. 4 it is apparent that for the substance *Ia,b* ($R = \text{CH}_3$) the configurations *E* and *Z* affect the p_{ij} values only slightly. In the substances of the types *II* and *III*, the characteristics of the π -electron distribution are negligibly dependent upon the geometry of the planar SCF models. At the same time the calculated π -bond orders indicate, however, that the formulas *I–III* do not comply satisfactorily with the localization of the multiple bonds in the molecules (Figs 4–6). The p_{ij} values for the bonds

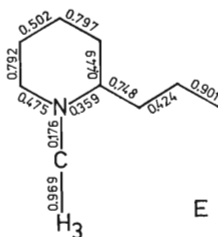
Fig. 3

Graphical Comparison of the Values of the ^{13}C Chemical Shifts in the NMR Spectrum of 1-Methyl-4-amino-3,3'-dicyano-3,5'-di(methoxycarbonyl)-2-propenylidene-1,2-dihydropyridine (*III*) Taken from Ref.¹¹ with the Calculated π -Electron Densities for the SCF Model *IIIa*

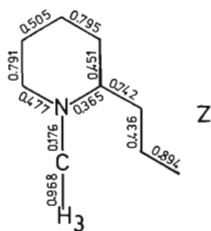
The connecting line of the electron densities is shown by solid line, chemical shifts by dashed line.



C(2)—C(3), C(4)—C(5), C(6)—N(1), and C(1')—C(2') are higher than as would correspond to the localization of the multiple bonds in the sense of the classical formula *I*. The introduction of the additional substituents R² to R⁶ in the substances *II* and *III* lowers most markedly the high order of the C(2')—C(3') π -bond from the value 0.901, which may be the cause of the tendency of the parent compound *I* to polymerization, to the considerably lower values 0.759 and 0.763, respectively. Between



E



Z

FIG. 4

SCF π -Electron Distribution at the Bonds of the *E* and *Z* Isomers of 1-Methyl-2-propenylidene-1,2-dihydropyridine (*Ia,b*) in the S_0 State

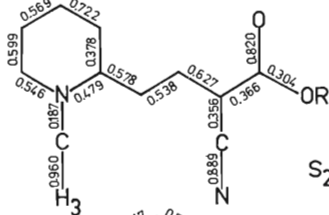
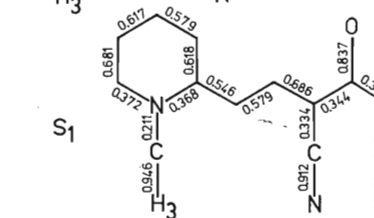
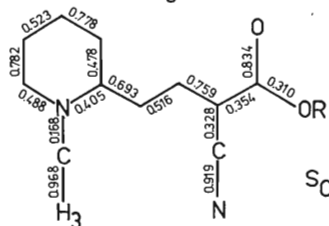
S₂S₁S₀

FIG. 5

π -Electron Distribution at the Bonds in the SCF Model *Iia* (R = CH₃) for S_0 , S_1 , and S_2 States

the other positions, too, the extreme p_{ij} values are commonly lowered and thus the π -delocalization becomes more pronounced. In this connection, the relatively low C=O bond order 0.834 in the R^3 substituent is remarkable; this is also reflected by the IR spectrum of the substance *II* ($R^1 = \text{CH}_3$, $R^3 = \text{CO}_2\text{CH}_3$), where the highest wavenumber of the vibrational modes of the conjugated skeleton is 1679 cm^{-1} . The fact that even the presence of the substituent R^6 ($p_{\text{CO}} = 0.851$) in the substance *III* ($R^1 = \text{CH}_3$, $R^3 = R^6 = \text{CO}_2\text{CH}_3$) does not shift the "carbonyl" absorption above 1700 cm^{-1} is ascribed to the occurrence of an intramolecular hydrogen bond between the carbonyl group and the amino group in the positions 4 and 5, existing under the conditions of the experiment.

The situation in the first and the second excited states, S_1 and S_2 , was approximated in accordance with the data of Table II by the configurations $\psi_{1-1'}$ and $\psi_{1-2'}$, respectively. We found the changes in the π -electron distribution to be similar for all the examined SCF models *Ia-IIIc*; they are shown in Fig. 5 for the structure *IIa*. It is apparent that the π -delocalization represented by the p_{ij} values is not in principle different in the two excited states. In the S_1 state the most weakened is the π -character of the bonds in the grouping C(6)—C(2) ($p_{\text{NC}} = 0.372$ and 0.368 , respectively), in the S_2 state this occurs with the C(2)—C(3) bond, where $p_{23} = 0.378$. Characteristic is also the partial "levelling" of the p_{ij} values in the fragment C(2)—C(1')—C(2')—C(3') corresponding to a deepening of the π -delocalization in the chain. On the whole it can be stated that the π -electron structures of the excited states S_1 and S_2 differ little from the π -electron distribution in the ground state S_0 . From this it can be inferred that also the chemical behaviour of the substances of the types *I-III* will be similar in darkness and during interaction with photons of the

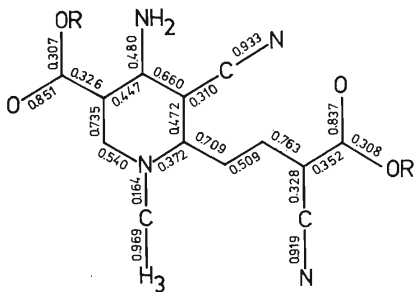


FIG. 6

π -Electron Distribution at the Bonds in the SCF Model *IIIa* ($R = \text{CH}_3$) in the S_0 State

visible light. This finding is in accordance with our experience that the substances *II* and *III* are quite stable when stored in daylight in common laboratory conditions, irrespective of their state of aggregation.

CONCLUSION

The intense orange to red colour of the substances *II* ($R^1 = \text{CH}_3$ and $R^2 = \text{CH}_3$ or C_2H_5) and *III* ($R^2 = R^6 = \text{CO}_2\text{CH}_3$) is explained according to the PPP calculations by the absorption transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ of the $\pi \rightarrow \pi^*$ type. The π -electron distribution does not change appreciably during these transitions, which is in accordance with the stability of the substances *II* and *III* towards light. The stereoisomeric 2-propenylidene-1,2-dihydropyridines *Ia,b* ($R = \text{H}$ or alkyl), so far not described, should display a blue shift of the long-wavelength absorption, and probably also an enhanced reactivity of the terminal double bond of the side chain.

We wish to thank Dr P. Trška for the measurement of the NOE of the substance II, and Mrs Z. Donnerová and Mrs M. Lutišánová for technical assistance. Our thanks are also due to the staff of the Central Laboratories of this Institute for the spectral measurements.

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