

ELECTRONIC AND MASS SPECTRA OF 2,6-DISUBSTITUTED PHENYL  
AND 2-STYRYL DERIVATIVES OF 3,5-DICYANOPYRIDINES  
AND THEIR 1,4-DIHYDROANALOGUES\*

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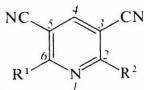
Ultraviolet and visible absorption spectra of the compounds *I* to *III* and their 1,4-dihydro-derivatives *IV* to *VI* have been confronted with the theoretical spectral characteristics calculated by the PPP method. 2- and 6-substituents effect on the character of the studied chromophores in the region of their singlet-singlet  $\pi-\pi^*$  transitions is discussed. Probable conformations and fragmentation mechanism after the electron impact at 70 eV are discussed for the compounds *II*, *III*, *V*, and *VI*.

In our previous report we showed<sup>1</sup> that ultraviolet absorption spectra of the compounds *II* and *V*, especially position of their long-wave absorption band, can be interpreted satisfactorily on the basis of simple HMO models. The present paper deals with an explicit calculation of the spectral characteristics by the PPP procedure, the study being extended by analogous investigation of spectra of bis-2-styryl derivatives *III* and *VI* and 2,6-diphenyl derivatives *I* and *IV*. We were especially interested in the extent of the change of the excitation character (described<sup>2,3</sup> for 3,5-dicyanopyridine and 3,5-dicyanodihydropyridine systems) due to conjugation with 2- and 6-substituents.

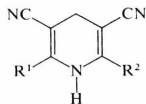
Preparation of the compounds *I*, *II*, *IV* and *V* was described<sup>1,4</sup>. Synthesis of the compounds *III* and *VI* from 2,6-dimethylpyridine (*VII*) is given in the present paper. Using the experience<sup>1</sup> that the monostyryl derivative *II* can be easily obtained from the compound *VII* by condensation with benzaldehyde, now the long-termed condensation in acetic anhydride was adopted for preparation of 2,6-bis(2-styryl) derivative *III*. The compound *III* was converted into the respective 1,4-dihydropyridine derivative *VI* by reduction with borohydride<sup>1,5</sup>. Structure of the new compounds *III* and *VI* (inclusive of *trans*-configuration at double bonds) was confirmed by PMR spectra. Spin coupling constants of 16 Hz were found for the protons in side olefin chains of the both compounds *III* and *VI*. These values correspond very well to those

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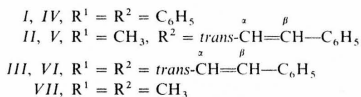
expected for *trans* arrangement at the double bond. For the compounds *III* and *VI* having two 2-styryl substituents at 2 and 6 positions no magnetic non-equivalence of olefinic protons  $H_\alpha$  in the vicinity of the heterocyclic ring was found, wherefrom it can be concluded that conformation of the both substituents  $R^2$  in the molecule will be the same.



I - III, VII



IV - VI



## EXPERIMENTAL

### Reagents

2,6-Diphenyl-3,5-dicyanopyridine<sup>4</sup> (*I*) m.p. 228–232°C (ref.<sup>4</sup> m.p. 228–232°C), 2-methyl-6-(2-styryl)-3,5-dicyanopyridine<sup>1</sup> (*II*) m.p. 223–224°C (ref.<sup>1</sup> m.p. 227–229°C), 2,6-diphenyl-1,4-dihydro-3,5-dicyanopyridine<sup>4</sup> (*IV*) m.p. 233–234°C (ref.<sup>4</sup> 233–234°C), 2-methyl-6-(2-styryl)-1,4-dihydro-3,5-dicyanopyridine<sup>1</sup> (*V*) m.p. 231–233°C (ref.<sup>1</sup> m.p. 233–234°C).

2,6-Bis(2-styryl)-3,5-dicyanopyridine (*III*). Mixture of 10 g (0.064 mol) dimethyl derivative *VII*, 22.9 g (0.25 mol) benzaldehyde and 8.9 g (0.067 mol) acetic anhydride was heated at 190 to 200°C under reflux for 100 h. The unreacted benzaldehyde was steam distilled, and the product was crystallized from chloroform (charcoal). Yield 13.9 g (42%) compound *III* m.p. 224–225°C. <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, ppm): —CH=C— 8.28 (d), γ-CH 8.10 (s), C<sub>6</sub>H<sub>5</sub> and —C=CH— 7.35–7.8 (m). For C<sub>23</sub>H<sub>15</sub>N<sub>3</sub> (333.4) calculated: 82.86% C, 4.54% H, 12.60% N; found: 82.48% C, 4.64% H, 12.30% N.

2,6-Bis(2-styryl)-1,4-dihydro-3,5-dicyanopyridine (*VI*). Suspension of 1.0 g (0.003 mol) compound *III* and 0.11 g (0.003 mol) NaBH<sub>4</sub> in 50 ml absolute ethanol was heated to 60°C. After the reaction subsided, the mixture was heated at 50°C for 5 min and left to stand overnight. Yellow crystals separated on addition of water were recrystallized from dimethyl sulphoxide, Yield 0.4 g (40%) of the product m.p. 248–250°C. <sup>1</sup>H-NMR spectrum (DMSO-d<sub>6</sub>, ppm): —NH— 8.24 (s), —CH=C— 6.76 (d), —CH<sub>2</sub>— 3.30 (s), C<sub>6</sub>H<sub>5</sub> and —CH=CH— 7.60–7.26 (m). For C<sub>23</sub>H<sub>17</sub>N<sub>3</sub> (335.4) calculated: 82.36% C, 5.11% H, 12.53% N; found: 82.22% C, 5.15% H, 12.66% N.

### Spectra

The <sup>1</sup>H-NMR were measured at 100 MHz with a Varian XL-100-15 spectrometer. Electronic spectra were measured with a Specord UV VIS (Zeiss, Jena) spectrophotometer in ethanolic

solutions of  $10^{-5}$  M concentration (Table I). The mass spectra were obtained with the use of a LKB 9000 (AB, Stockholm) spectrometer and a MS 9 (AEI, Manchester) apparatus at 70 eV and ion source temperature 40 and 70°C.

### Calculations

The calculations of theoretical electronic spectra were carried out by the standard PPP method<sup>6-8</sup> using an E 503 computer (author of the program is Dr J. Pancíř, J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague). The bicentric repulsion integrals were approximated according to Mataga and Nishimoto<sup>9</sup>. The parameters used are summarized in Table II. Ideal geometry of the system was considered with valence angles 120° (180° for nitrile group). The bond lengths in pyridine, dihydropyridine and benzene nuclei were taken 139 pm. For the other bonds the following values were used: C—C≡ 146 pm, C≡N 116 pm, C—C= 147 pm, —C=C— 134 pm.

## RESULTS AND DISCUSSION

*Electronic absorption bands.* The electronic absorption spectra of the earlier studied<sup>1</sup> compounds *II* and *V* showed characteristic features especially in the long-wave region due to connection of the basic 3,5-dicyanopyridine or -dihydropyridine chromophore with an extensive substituent at 2-position able of conjugation. It was possible to interpret satisfactorily<sup>1</sup> the position of the longest-wave absorption bands by comparison of the HMO excitation energies  $E(N \rightarrow V_1)$ . Now we were interested in the problem of evaluation of these results by the use of the more perfect PPP method, estimation of the type of electronic transitions and possible discussion of conformation of these rather complicated chromophores.

From Figs 1 and 2 it is obvious that the calculated positions of absorption bands of singlet-singlet  $\pi-\pi^*$  transitions of the compounds *I* to *VI* correspond quite well to the experimental envelope absorption curves. Hence it can be concluded that the

TABLE I  
Electronic Spectra of Compounds *I*—*VI*

Compound	$\tilde{\nu}_{\max} \cdot 10^{-3}, \text{ cm}^{-1} (\log \epsilon)$			
<i>I</i>	35.6 (4.48)	45.5 (4.30) <sup>a</sup>	48.5 (4.57)	
<i>II</i>	29.7 (4.10)	43.8 (4.23) <sup>a</sup>	48.8 (4.62)	
<i>III</i>	29.4 (4.56)	44.3 (4.35) <sup>a</sup>	48.9 (4.59)	
<i>IV</i>	27.4 (4.15)	37.9 (4.27)	41.2 (4.34)	48.8 (4.54)
<i>V</i>	27.0 (3.50)	33.7 (4.47)	44.5 (4.14) <sup>a</sup>	48.8 (4.31)
<i>VI</i>	27.5 (3.71) <sup>a</sup>	32.3 (4.71)	44.2 (4.32) <sup>a</sup>	48.9 (4.56)

<sup>a</sup> Inflection.

studied chromophores exhibit (in ultraviolet and visible spectral regions) only absorptions due to singlet-singlet  $\pi$ - $\pi^*$  transitions. A more detailed discussion of the results is complicated by possibility of various conformations of side chains at 2 and 6 positions and by the choice of a suitable  $\pi$ -SCF model for dihydropyridine ring. Our further investigation was focused only on planar conformations of the compounds *I* to *VI*, and the inductive model tested earlier<sup>3</sup> was used for dihydropyridine nucleus.

In the case of the compounds *I* and *IV* the conformation problem can be eliminated by considering the conformation of 2,6-phenyl groups to be coplanar (or nearly so) with heterocyclic ring. Comparison of experimental absorption curves in Fig. 1 shows a very good agreement with the calculated transitions for the pyridine derivative *I*. The dihydropyridine *IV* shows a good agreement for the long-wave maximum, the agreement being not very good for the other transitions. The choice of model is more complicated for the compounds *II*, *III*, *V*, *VI* containing 2,6-styryl groups. According to PMR measurements we considered only the *trans* configuration of  $-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ . Assuming planar arrangement of the molecules *II*, *III*, *V*, *VI*, two conformations (*syn* and *anti*) must be taken into account for the styryl group. *E.g.* the conformers *II*<sub>s</sub> and *II*<sub>a</sub> for the *trans* isomer of the compound *II*. The presence of two styryl groups (at 2 and 6 positions) allows two symmetrical conformations *syn*, *syn* (*s*, *s*) and *anti*, *anti* (*a*, *a*) and one unsymmetrical *syn*, *anti* (*s*, *a*). Although this *s*,*a*-conformation seems to be excluded by PMR spectra, it was involved in the calculations. For all the studied styryl derivatives *II*, *III*, *V* and *VI* a good agreement between the calculated *S-S*  $\pi$ - $\pi^*$  transitions with the experimental absorption curves was obtained. The agreement was practically the same regardless

TABLE II  
The Standard Parameters Used in the PPP Calculations

Atom	$I_p$ , eV	$A$ , eV	Ref.	Bond	$E^a$	Ref.
$\text{C}(sp^2)$	11.16	0.03	10	$\text{C}(sp^2)-\text{C}(sp^2)^b$	1.0	—
$\text{C}(sp^2)^c$	10.70	-0.25	3	$\text{C}(sp^2)-\text{C}(sp^2)^d$	1.1	—
$\text{C}(sp)$	11.18	0.10	10	$\text{C}(sp^2)-\text{C}(sp)^e$	0.9	—
$\text{N}(sp^2)^f$	14.12	1.78	10	$\text{C}(sp^2)-\text{C}(sp)$	0.9	3
$\text{N}(sp)$	14.18	1.66	10	$\text{C}(sp^2)-\text{N}(sp^2)^f$	1.0	2
$\text{N}(sp^2)^g$	27.50	9.20	11	$\text{C}(sp^2)-\text{N}(sp^2)^g$	0.8	11
				$\text{C}(sp)-\text{N}(sp)$	1.4	2

<sup>a</sup> In  $\beta$  units ( $\beta = -2.388$  eV), <sup>b</sup> "aromatic" bond, <sup>c</sup> positions 3 and 5 of dihydropyridine ring, <sup>d</sup> double bond in styryl chain, <sup>e</sup> single bond, <sup>f</sup> in pyridine ring, <sup>g</sup> in dihydropyridine ring.

of conformation of styryl group (Figs 1 and 2). Hence comparison of the calculated characteristics with experiment cannot decide about the predominant conformation in the measured solution. In connection therewith we compared the SCF  $\pi$ -electron energies of the conformers of the compounds *II*, *III*, *V* and *VI* (Table IV), and it turned out that *syn* conformation is more favourable than *anti* by 0.12 eV (for the compounds *II* and *III*) and by 0.08 eV (for the dihydropyridines *V* and *VI*). Hence it can be presumed that *syn* conformation will be preferred, if only  $\pi$ -electron contribution is considered.

When following the weights of the configuration it is possible to observe some differences from the regularity described for simple cyanopyridine chromophores<sup>2</sup>

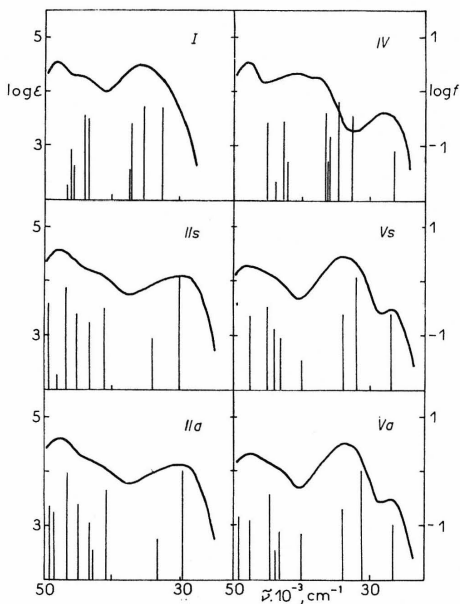


FIG. 1

Comparison of Experimental Extinction Curves with Theoretical Calculated Transitions for Compounds *I*, *IV*, *II* and *V*

and, on the contrary, some agreement with the behaviour of 3,5-dicyanodihydropyridine chromophore<sup>3</sup>. In the region of long-wave bands a significant difference was described<sup>2,3</sup> between the abundance of the individual configurations in the case of chromophores with pyridine ring and those of dihydropyridine type, which is manifested by that the long-wave bands of pyridine derivatives are combinations of more configurations with relatively high weights, whereas in the case of dihydropyridines practically only one dominant configuration is present. The first transition of the pyridine chromophore represents a combination of configurations 1-2' and 2-1', the configuration 1-1' being significant only in the second transition. Introduction of substituents able of conjugation in the positions 2 and 6 of the compounds *I* to

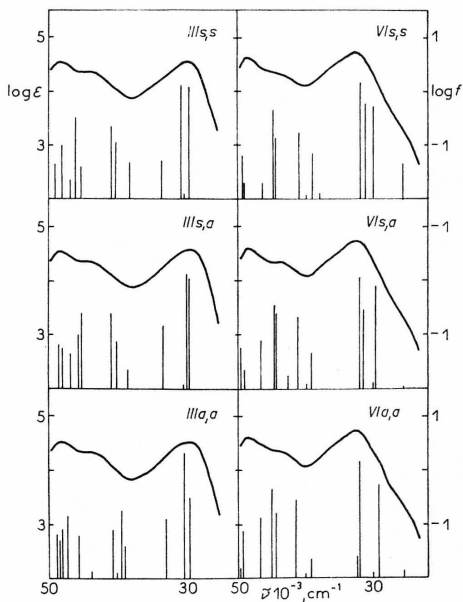


FIG. 2

Comparison of Experimental Extinction Curves with Theoretical Calculated Transitions for Compounds *III* and *VI*

TABLE III

The Calculated Characteristics of the Two Longest-Wave Transitions in Electronic Spectra of Compounds I–VI

Compound	$\tilde{\nu} \cdot 10^{-3}, \text{cm}^{-1}$	$\lambda, \text{nm}$	$\log f$	Configuration	Weight, %
<i>I</i>	32.60	306.8	-0.291	1-2'	89.5
	33.26	300.7	-0.280	1-1'	93.1
<i>II<sub>s</sub></i>	29.99	333.4	0.088	1-1'	94.3
	33.85	295.4	-1.060	1-2'	65.9
<i>II<sub>a</sub></i>	29.52	338.7	0.014	1-1'	95.4
	33.27	300.6	-1.248	1-2'	68.3
<i>III<sub>s,s</sub></i>	29.36	340.6	0.072	1-2'	84.0
	30.27	330.3	0.112	1-1'	90.9
<i>III<sub>s,a</sub></i>	29.53	338.5	0.043	1-1'	57.1
				1-2'	28.5
	29.89	334.5	0.120	1-2'	54.8
<i>III<sub>a,a</sub></i>				1-1'	31.6
	29.31	341.2	-0.493	1-1'	89.6
	30.07	332.5	0.337	1-2'	81.8
<i>IV</i>	26.69	374.6	-1.109	1-1'	95.6
	32.56	307.1	-0.435	1-2'	96.2
<i>V<sub>s</sub></i>	26.89	371.7	-0.692	1-1'	85.6
	31.86	313.9	0.086	2-1'	80.9
<i>V<sub>a</sub></i>	26.69	374.6	-0.979	1-1'	93.7
	31.33	319.1	0.011	2-1'	82.7
<i>VI<sub>s,s</sub></i>	25.66	389.7	-1.338	1-1'	93.0
	29.96	333.7	-0.278	1-2'	95.1
<i>VI<sub>s,a</sub></i>	25.70	389.1	-2.223	1-1'	86.8
	29.71	336.6	-0.091	1-2'	77.8
	25.66	389.7	-1.847	1-1'	89.6
<i>VI<sub>a,a</sub></i>	29.29	341.4	-0.277	1-2'	72.0
				2-1'	26.9

TABLE IV

SCF  $\pi$ -Electron Energies of Conformers of Compounds II, III, V and VI

Compound	$E^{\text{SCF}}, \text{eV}$	Compound	$E^{\text{SCF}}, \text{eV}$
<i>II<sub>s</sub></i>	-241.463	<i>V<sub>s</sub></i>	-247.610
<i>II<sub>a</sub></i>	-241.345	<i>V<sub>a</sub></i>	-247.535
<i>III<sub>s,s</sub></i>	-343.564	<i>VI<sub>s,s</sub></i>	-349.720
<i>III<sub>a,s</sub></i>	-343.447	<i>VI<sub>a,s</sub></i>	-349.644
<i>III<sub>a,a</sub></i>	-343.328	<i>VI<sub>a,a</sub></i>	-349.568

*VI* results in a marked change. In long-wave transitions practically one dominant configuration with high weight is observed (Table III); for the longest-wave transition this configuration is always 1-1' except for the compounds *I* and *III*<sub>s</sub>, *s*. The exception for the compound *III*<sub>s</sub>, *s* is obviously due to small energy difference between the longest-wave transitions (Table III). In the case of the compound *I* the influence of phenyl groups will probably be smaller than that of the styryl groups in the compounds *II* and *III*, which results in a greater similarity of the compound *I* with the non-substituted 3,5-dicyanopyridine. The compounds *II* to *VI* (both pyridine and dihydropyridine derivatives) behave to a certain extent as the non-substituted 1,4-dihydro-3,5-dicyanopyridine<sup>3</sup>. This fact explains the good correlation of energies of the longest-wave bands with the HMO excitation energies  $E(N \rightarrow V_1)$  which we found for an analogous series of compounds<sup>1</sup>.

*$\pi$ -Electron distribution in ground and excited states.* Information obtained from detailed analysis of the excitation process, especially relation between  $\pi$ -electron distribution of the ground and the excited states, turned out a significant factor in description of behaviour of the investigated chromophores. We dealt with the first and the second excited states  $S_1$  and  $S_2$  as the poorest energetically for which only one dominant configuration is significant. Especially we were interested in the relations between changes of electron distribution, configurations, chromophore type and its conformation.

The relation between chromophore type and dominant configuration on the one hand and change of electron distribution on the other hand turned out to be most important. In the case of compounds containing pyridine nucleus, 1-1' and 1-2' are the dominant configurations in the first and the second transitions ( $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow S_2$ ). In all the cases electron transfer from the styryl groups towards pyridine nucleus predominates, especially to the positions 1 and 4 and 6 for the configuration 1-2' and to the position 2 for the configuration 1-1'. The situation is illustrated in Table V for the compound *III*<sub>s</sub>, *s*. An electron density increase in nitrile groups is observed in configuration 1-1', whereas the reverse is true for the configuration 1-2' (Table V). Regardless of the dominant configuration the bond orders change towards higher delocalization, *i.e.* the bond orders of the formally multiple bonds are decreased, those of single bonds being increased. A reverse situation is encountered with chromophores having dihydropyridine ring. Generally the configurations 1-1' and 1-2' show a decrease in  $\pi$ -electron densities in 1, 3 and 5 positions of the ring, and, on the contrary, the electrons are shifted towards the styryl groups or also towards the nitrile group in the case of the configuration 1-1'. (Table V, the compound *VI*<sub>s</sub>, *s*). The changes observed in 1,4-dihydro-3,5-dicyanopyridine ring are practically the same<sup>3</sup> as those in the chromophore lacking styryl or phenyl groups at 2 and 6 positions. Only are the changes less marked in the case of these more extensive systems. The bond order changes are the same as in the pyridine compounds. For the compounds *V*<sub>s</sub>

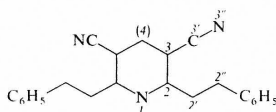


and  $Va$  the dominant configuration in the second transition  $S_0 \rightarrow S_2$  is the configuration 2-1' which can be stated to have opposite effect on  $\pi$ -electron density changes as compared with the configuration 1-2'.

*Fragmentation of molecules.* Mass spectra of the investigated 2-methyl-6-styryl- (II) and 2,6-distyryl-3,5-dicyanopyridine (III) exhibit (Table VI) an intensive ion sort  $[M - 1]^+$  corresponding to stable azaphenanthrene cation  $a$ . From Scheme 1 it can be seen that this ion sort is formed by intramolecular cyclization in the *ortho* position of the benzene ring of the styryl group with pyridine nitrogen atom. A similar

TABLE V

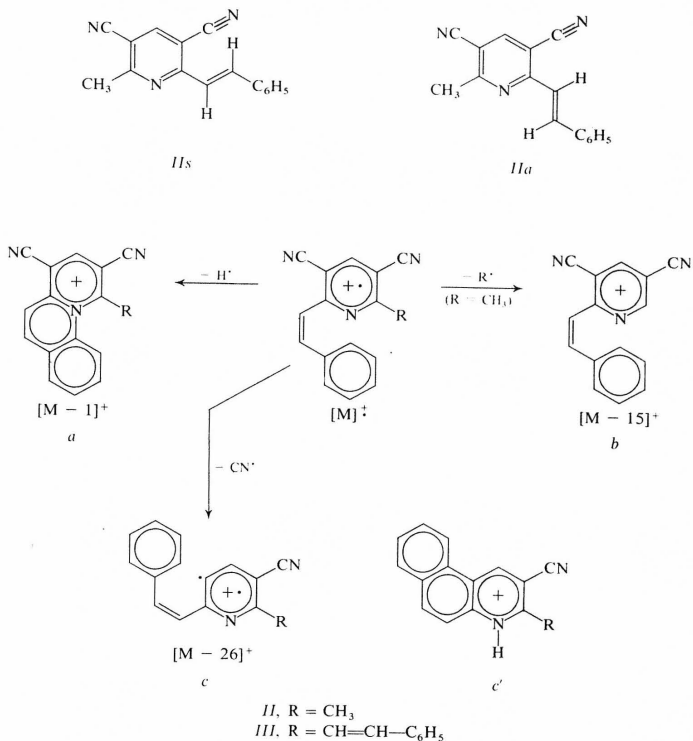
$\pi$ -Electron Distribution Changes of Compounds  $III_{s,s}$  and  $VI_{s,s}$  in the First Two Longest-Wave Transitions



Compound	Position	Electron densities <sup>a</sup>		Bond	Bond orders <sup>a</sup>	
		$\Delta q_{(1-1')}$	$\Delta q_{(1-2')}$		$\Delta p_{(1-1')}$	$\Delta p_{(1-2')}$
$III_{s,s}$	1	0.002	0.145	1-2	-0.004	0.092
	2	0.057	0.017	2-2'	0.122	0.109
	2'	-0.037	-0.024	2'-2''	-0.151	-0.154
	2''	0.012	0.002	2''-Ph	0.079	0.087
	Ph	-0.045 <sup>b</sup>	-0.019 <sup>b</sup>	2-3	-0.167	-0.054
	3	-0.027	-0.090	3-3'	0.055	0.017
	3'	0.027	0.007	3'-3''	-0.040	-0.012
	3''	0.010	-0.026	3-4	-0.001	-0.038
$VI_{s,s}$	4	0.001	0.125			
	1	-0.213	-0.147	1-2	0.103	0.052
	2	0.040	0.000	2-2'	0.077	0.086
	2'	0.032	0.074	2'-2''	-0.072	-0.117
	2''	0.057	0.068	2''-Ph	0.025	0.060
	Ph	0.026 <sup>b</sup>	0.109 <sup>b</sup>	2-3	-0.211	-0.157
	3	-0.092	-0.154	3-3'	0.070	-0.034
	3'	0.037	0.018	3'-3''	-0.054	-0.026
3''	0.000	-0.039				

<sup>a</sup> The index denotes the dominant configuration; <sup>b</sup> overall change of electron density in phenyl ring.

cyclization was observed with styrylarenes<sup>12</sup>, styrylpyrazoles<sup>13</sup> and, recently, with 6-styrylpyridinedicarboxylic acids and their esters<sup>14</sup>. Mass spectrum of the compound *II* contains an intensive ion sort *b* of the composition  $[M - 15]^+$  corresponding to elimination of methyl radical from the position 2 of the molecular ion. For this process a metastable transition  $m/e$  195.8 was observed ( $245 \rightarrow 219 + 15$ ; calculated  $m/e$  195.7). No analogous fragment corresponding to splitting off of styryl residue from the compound *III* was observed. A medium intensive ion sort *c*



SCHEME 1

$[M - 26]^+$  is formed by splitting off of CN radical from molecular ion. For this ion two alternative structures can be presumed, an open one *c* and a cyclic one *c'*. The thermodynamically more stable fragment *c* necessitates formation of a bond between *ortho* position of phenyl residue and  $\beta$  position of pyridine nucleus which got free after elimination of cyano group.

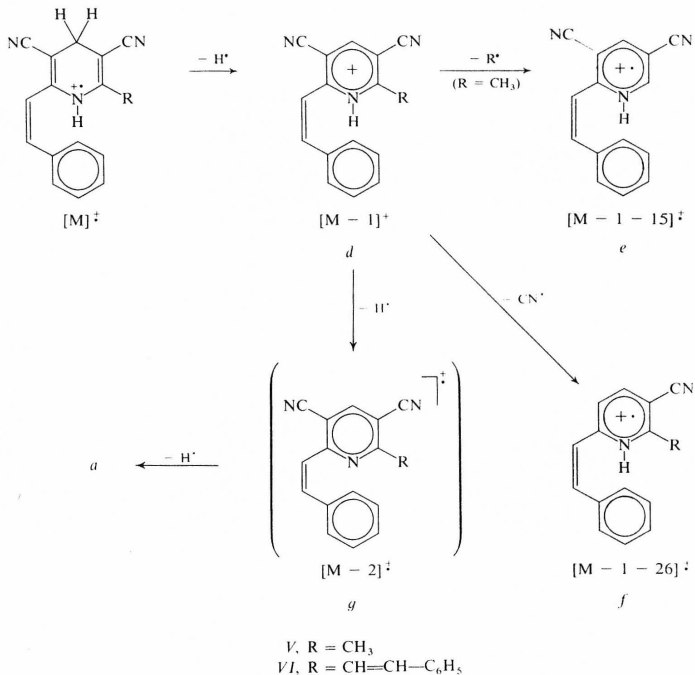
In accord with our previous findings<sup>15</sup> the dominating process in fragmentation of the dihydropyridines *V* and *VI* consists in elimination of hydrogen radical from the position 4 to form stable pyridine cation *d* with the mass  $[M - 1]^+$ . From Scheme 2 it is obvious that the ions  $e[M - 1 - 15]^+$  and  $f[M - 1 - 26]^+$  are formed by analogous mechanism as those from the pyridine derivatives *II* and *III*. Gradual aromatization of dihydropyridine nucleus is remarkable, the pyridine cation *d* giving most probably azaphenanthrene ion *a* by successive splitting off of two further hydrogen atoms. The ion sort  $[M - 2]^+$  has probably the open structure *g*. We measured the mass spectra at various temperatures with two spectrometers to eliminate the possibility of aromatization of dihydropyridine ring under the conditions

TABLE VI

Mass Spectra of the Compounds *II*, *III*, *V*, *VI* (70 eV)

For description of ion sorts see Schemes 1 and 2. The Table gives the ion sorts with integer values *m/e* and abundance higher than 5% rel. int., others are given only if they have any diagnostic importance.

Mass	<i>II</i>		<i>V</i>		<i>III</i>		<i>VI</i>	
	<i>m/e</i>	% r.i.	<i>m/e</i>	% r.i.	<i>m/e</i>	% r.i.	<i>m/e</i>	% r.i.
$M + 1$	246	19.1	248	9.7	334	27.2	336	10.2
$M$	245	100.0	247	54.4	333	100.0	335	38.5
$M - 1$	244 <sup>a</sup>	56.5	246 <sup>d</sup>	100.0	332 <sup>a</sup>	33.3	334 <sup>d</sup>	100.0
$M - 2$	243	8.2	245	20.4	331	10.5	333	34.6
$M - 3$	242	3.9	244 <sup>a</sup>	13.5	330	7.2	332 <sup>a</sup>	10.3
$M - 15$	230 <sup>b</sup>	11.3	232	4.8	—	—	—	—
$M - 1 - 15$	229	—	231 <sup>e</sup>	10.7	—	—	—	—
$M - 26$	219 <sup>c</sup>	22.4	221	2.4	307 <sup>e</sup>	21.8	309	5.8
$M - 1 - 26$	—	—	220 <sup>f</sup>	8.3	306	4.6	308 <sup>f</sup>	20.8
$M - 79$	—	—	—	—	254	10.8	256	—
$M - 1 - 79$	—	—	—	—	253	—	255	11.5
$M - 103$	—	—	—	—	230	4.4	232	3.8
$M - 1 - 103$	—	—	—	—	229	3.8	231	9.6
<i>m/e</i> 91	—	2.5	—	2.6	—	7.9	—	30.8
<i>m/e</i> 77	—	8.2	—	6.9	—	12.8	—	17.3
<i>m/e</i> 63	—	5.5	—	2.7	—	3.6	—	5.8
<i>m/e</i> 51	—	8.2	—	4.2	—	8.4	—	11.2



SCHEME 2

of measurements. In all cases we obtained the same ion sorts in identical intensities. The nuclide-coupled ions in spectra of all the studied compounds *II*, *III*, *V* and *VI* agree with the suggested summary formulas. The ion sorts with the values  $m/e$  91 and  $m/e$  77 are due to tropylium  $[C_7H_7]^+$  and phenyl  $[C_6H_5]^+$  cations, respectively, and they are more intensive in the case of the distyryl derivatives *III* and *VI*.

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## REFERENCES

1. Skála V., Uhlová O., Kuthan J.: *This Journal* **40**, 1892 (1975).
2. Skála V., Kuthan J.: *This Journal* **35**, 2378 (1970).
3. Kuthan J., Skála V., Musil L.: *This Journal* **38**, 3479 (1973).
4. Kuthan J., Hakr E.: *This Journal* **32**, 1438 (1967).
5. Eisner U., Kuthan J.: *Chem. Rev.* **72**, 1 (1972).
6. Pople J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953).
7. Pariser R., Parr R. G.: *J. Chem. Phys.* **21**, 466 (1953).
8. Pariser R., Parr R. H.: *J. Chem. Phys.* **21**, 767 (1953).
9. Mataga N., Nishimoto K.: *Z. Phys. Chem. (Frankfurt am Main)* **13**, 140 (1957).
10. Hünze J., Jaffé H. H.: *J. Amer. Chem. Soc.* **84**, 540 (1962).
11. Pancíř J.: Private communication.
12. Johnstone R. A. W., Ward S. D.: *J. Chem. Soc. (C)* **1968**, 1805.
13. El Khadem H. S., Foltz R. L., Horton D.: *J. Heterocycl. Chem.* **11**, 575 (1974).
14. El Khadem H. S., Rateb L., Mokhtar H.: *J. Heterocycl. Chem.* **12**, 1299 (1975).
15. Paleček J., Kuthan J.: *This Journal* **40**, 2632 (1975).

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