

## $\pi$ -ELECTRONIC STRUCTURE AND ELECTRONIC SPECTRA OF METHYLATED 3,5-DICYANOPYRIDINES

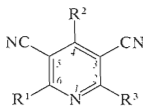
D. ILAVSKÝ and J. KUTHAN

Organic Chemistry Department,  
Slovak Institute of Technology, 800 00 Bratislava and  
Organic Chemistry Department,  
Prague Institute of Chemical Technology, 166 28 Prague 6

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Quantum-chemical interpretation is given of UV spectra of mono-, di-, and trimethylated 3,5-dicyanopyridines using the LCI method on the basis of HMO and SCF wave functions. Results of the both procedures (PPP and HMO-LCI) agree well with experiment. The both modifications agree also in qualities of individual transitions and weights of configurations. Influence of methyl group on 3,5-dicyanopyridine skeleton is followed by the electron density change.

In the previous papers reactivity of some alkylated 3,5-dicyanopyridines was studied on the basis of simple HMO method<sup>1</sup> along with the influence of the substituent position change on the reactivity of the skeleton towards<sup>2</sup> NaBH<sub>4</sub>. Now our attention has been focused especially on the interpretation of UV spectra by the method of limited configuration interaction (LCI). Most often theoretical calculations of electronic spectra of  $\pi$ -conjugated systems use SCF molecular orbitals<sup>3</sup> as the basis, less often they use the modified CNDO/2 (ref.<sup>4</sup>) or INDO MO (ref.<sup>5</sup>) and only very rarely heterocyclic systems were studied by the HMO-LCI method<sup>6</sup>. The derivative *I* was studied before<sup>7</sup> along with polycyanopyridines, the results of theoretical UV spectra being analogously confronted. The PPP method was also used for a study of influence of methyl group on UV spectra of the methylated pyridines<sup>8</sup>. This work makes use of the cited pieces of knowledge<sup>7,8</sup> for the study of electronic spectra of structurally more complex derivatives *II*–*VI* by the PPP and HMO-LCI procedures. Survey of the studied compounds see formulae *I*–*VI*.



- I*, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H  
*II*, R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = R<sup>3</sup> = H  
*III*, R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = CH<sub>3</sub>  
*IV*, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>, R<sup>3</sup> = H  
*V*, R<sup>1</sup> = R<sup>3</sup> = CH<sub>3</sub>, R<sup>2</sup> = H  
*VI*, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub>

## CALCULATIONS AND PARAMETERS

The HMO calculations were carried out by the usual way<sup>9,10</sup> using the parameters from the previous works<sup>1,7</sup> (for the pyridine ring nitrogen atom  $\delta_N = 0.5$ ,  $\rho_{CN} = 1.0$ ; for nitrile group  $\delta_N = 0.5$ ,  $\rho_{CN} = 1.4$ ). Hyperconjugation model of methyl group was used for the calculation ( $\delta_{C(H_3)} = -0.1$ ,  $\rho_{C\equiv(H_3)} = 3.0$ ;  $\delta_{H_3-(C)} = -0.5$ ,  $\rho_{C-CH_3} = 0.8$ , and  $\delta_{C-CH_3} = -0.1$ ). The SCF models of the studied compounds were calculated in the Pople-Pariser-Parr version<sup>11-13</sup>. The elements of F-matrix were expressed according to Pople, and monocentric Coulomb integrals were approximated by ionization potential. The values of ionization potentials and electron affinities were taken from refs<sup>4,5</sup>. The resonance integrals are expressed in  $\beta$  units ( $\beta = -2.388$  eV). For the SCF calculation the hyperconjugation model of methyl group was used, too, the following geometry being considered: heteroaromatic ring as regular hexagon with valence angles  $120^\circ$  and bond lengths  $0.139$  nm. The other values used in the calculation are summarized in Table I. The bicentric repulsion integrals were applied according to Mataga and Nishimoto<sup>14</sup>. For the calculation 25 monoexcited configurations were used. In the calculation the intensity is characterized by logarithm of oscillator strength ( $\log f$ ). In Table II the empirical relation between the oscillator strength and the extinction coefficient was used  $\log \epsilon = \log f + 4$ . This relation allows to interpret relatively well the band intensities with respect to the calculation. The HMO calculation was carried out with the computer Tesla 270, and the HMO-LCI and PPP calculations were carried out with the computer Elliott 503.

## EXPERIMENTAL

The derivatives studied were synthesized according to the previous work<sup>1</sup>. All the substances were purified by sublimation in vacuum. The UV spectra were measured with a Specord UV VIS spectrophotometer (Zeiss, Jena) in ethanolic  $4 \cdot 10^{-5} M$  solutions. The spectral data are summarized in Table II.

TABLE I  
SCF Calculation Parameters

For zero iteration in all the SCF calculations  $h_x = 0$ .

Atom	$I$ eV	$A$ eV	Bond	$k_{CX}$	$Z$	$r_{CX}$ A
$C(sp^2)$	11.16	0.03	$C(sp^2)-C(sp^3)$	1.0	1	1.39
$N(sp^2)$	14.12	1.78	$N(sp^2)-C(sp^2)$	1.0	1	1.39
$C(sp)$	11.19	0.10	$C(sp^2)-C(sp)$	0.9	1	1.46
$N(sp)$	14.18	1.66	$C(sp)-N(sp)$	1.4	1	1.16
$C(sp^3)$	11.42	0.58	$C(sp^2)-C(sp^3)$	0.51	1	1.52
$H_3\equiv(C)$	9.50	0.0	$H_3-(C)$	1.25	1	1.10

TABLE II  
Comparison of Calculated and Experimental Spectral Characteristics of Compounds I-III

Com- pound	$E \cdot 10^{-3}$ $\text{cm}^{-1}$		HMO-LCI		$E \cdot 10^{-3}$ $\text{cm}^{-1}$		SCF-LCI		Experiment		
	$\log f + 4$	$i-j^b$	% <sup>c</sup>	$E \cdot 10^{-3}$ $\text{cm}^{-1}$	$\log f + 4$	$i-j^b$	% <sup>c</sup>	$E \cdot 10^{-3}$ $\text{cm}^{-1}$	$\log \epsilon$	$E \cdot 10^{-3}$ $\text{cm}^{-1}$	$\log \epsilon$
I	36.64	2.9	1-2'	62.97	2.80	1-2'	64.96	36.36	3.23		
			2-1'	25.42							
	44.47	3.51	1-1'	84.27	3.44	1-1'	83.82	44.44	3.99		
			2-2'	11.96		2-2'	15.39				
II	48.16	5.23	2-1'	62.27	3.82	2-1'	58.09	47.35	4.58		
			1-2'	32.41		1-2'	29.66				
	36.97	3.03	1-2'	66.65	3.00	1-2'	61.86	34.84 <sup>d</sup>	3.38		
			2-1'	24.82		2-1'	24.78	35.88	3.40		
III	43.22	3.65	1-1'	89.16	3.66	1-1'	84.46	43.94	4.11		
	47.74	4.24	2-1'	62.85	3.82	2-1'	50.76	47.92	4.46		
			1-2'	30.43		1-2'	27.49				
	36.88	2.60	1-2'	59.89	2.49	1-1'	58.64	35.20 <sup>d</sup>	2.82		
III			2-1'	30.53		2-2'	31.41	38.46	3.01		
	44.08	2.06	1-1'	66.81	1.56	2-1'	64.63	44.44	4.07		
			2-2'	30.79		1-2'	33.47				
	46.92	5.22	2-1'	60.00	3.88	2-2'	59.44	47.90	4.46		
		1-2'	36.74		1-1'	34.36					
				3.99	1-2'	62.13					
					2-1'	27.17					

IV	36.88	2.85	1-2'	64.16	36.69	2.83	1-2'	32.65	34.90 <sup>a</sup>	3.18
			2-1'	28.38			1-1'	30.65	36.10	3.28
							2-1'	17.07		
	42.08	3.43	1-1'	78.95	41.35	3.19	1-1'	40.48	43.17	4.12
			2-2'	18.49			1-2'	27.61		
							2-1'	17.84		
V	46.54	4.22	2-1'	62.62	44.78	4.00	2-2'	49.87	46.95	4.51
			1-2'	32.38			1-1'	18.72		
					45.61	4.06	2-1'	41.46		
	37.02	3.13	1-2'	70.65	36.57	3.21	1-2'	73.11	34.41 <sup>a</sup>	3.49
			2-1'	23.48			2-1'	20.73	35.56	3.55
							1-1'	90.49	42.41	4.06
VI	42.13	3.69	1-1'	91.02	40.72	3.66	1-1'	71.53	47.35	4.76
	47.43	4.26	2-1'	66.57	46.11	4.22	2-1'	21.37		
			1-2'	27.53			1-2'			
	36.54	2.94	1-2'	67.08	36.66	3.02	1-2'	69.34	34.63 <sup>a</sup>	3.35
			2-1'	26.93			2-1'	26.63	35.87	3.37
							1-1'	79.03	41.66	4.07
VII	41.75	3.54	1-1'	84.21	40.42	3.37	1-1'	18.90		
			2-2'	13.91			2-2'			
	46.14	4.24	2-1'	64.95	44.65	3.02	2-2'	68.53		
			1-2'	30.95			1-1'	14.87		
					44.82	4.18	2-1'	65.94		
							1-2'	28.00		
48.33	3.90	2-2'	84.15	48.33	2.45	3-1'	60.62	47.62	5.00	
						1-3'	32.92			

<sup>a</sup> Inflection; <sup>b</sup> dominant transition from the *i*-th bonding MO to the *j*-th antibonding MO; <sup>c</sup> weight of the transition.

## RESULTS AND DISCUSSION

HMO and SCF data. In contrast to the previous paper<sup>1</sup> (HMO 1) we have used the hyperconjugation model for methyl group (HMO 2). Fig. 1 gives the molecular diagrams of the compound VI obtained by the both procedures along with SCF calculations. Parametrization change in HMO procedure does not affect significantly the electron density distribution in the studied skeleton. The hyperconjugation model increases slightly the  $\pi$ -bond orders in heteroaromatic ring. In the case of SCF electron densities and bond orders the electron delocalization in the skeleton makes itself felt even more markedly, however, the parallel between the followed calculation values is maintained. Fig. 2 shows this trend for the compound II. Increasing number of methyl groups increases additively the  $\pi$ -electron energy of the studied molecule, the increment being about 25 eV per one methyl group. Electron density of the electronegative nitrogen atoms in nitrile group and pyridine ring change similarly.

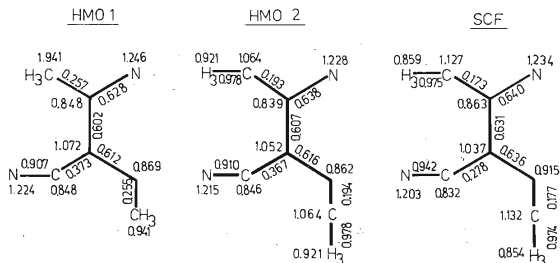


FIG. 1  
Molecular Diagram of Compound VI

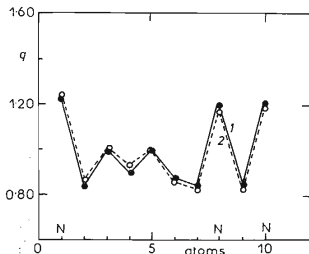


FIG. 2  
Comparison of Electron Density Values of 2-Methyl-3,5-dicyanopyridine (— HMO calculation, - - - SCF calculation)

Fig. 3 represents the electron density changes at individual atoms, the circle magnitude corresponding to the relative positive (empty circle) or negative change (full circle). Introduction of methyl group in 3,5-dicyanopyridine skeleton causes practically no change in electron density at *meta*-position. All the electron density changes refer to the compound *I* the unsubstituted skeleton of which was taken as the reference compound. Change from the heteroatom model of the methyl group to the hyperconjugation model expresses equally well the position of nucleophilic attack on the basis of the nucleophilic superdelocalizability  $S_n$  and nucleophilic localization energy  $L_n$ , as it was given in ref.<sup>1</sup>.

**UV Spectra.** Absorption UV spectra of the compounds studied (Table II) show typical aromatic character with vibration structure of the band in the long-wave region which is affected by number and positions of the methyl groups present. Intensity of the longest-wave band is substantially lower ( $\log \epsilon = 3.0$  to  $3.5$ ) than that of the bands in the short-wave region ( $\log \epsilon = 4.0$  to  $4.5$ ). Methyl groups cause the longest-wave band to shift bathochromically by about 5 to 10 nm. The medium band shows a bathochromic shift only with the compounds *V* and *VI*, namely by about 10 nm. In the other cases the shift is small (2 to 3 nm).

The attempted correlation of the longest-wave band wave number with the theoretically computed  $N \rightarrow V_1$  transition energy was statistically insignificant, which was confirmed also by the configuration weights analysis of this band, as the transition is not a so called pure one. With all the compounds *II* to *VI* a good agreement with experiment was obtained (Table II), especially so for the band positions. If the compounds contain methyl group at 4-position, PPP calculation gives always two bands in the short-wave region involving the transitions  $1-1'$ ,  $1-2'$ ,  $2-2'$ , and  $2-1'$  which are shifted bathochromically as compared with the experimental values (see the compounds *III*, *IV*, and *VI*). In Fig. 4 it can be seen that the both bases give parallel results for the other derivatives (*I*, *II*, and *V*), too. Analysis of the weights of configurations

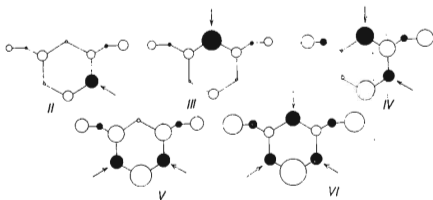


FIG. 3. Influence of Methyl Groups on  $\pi$ -Electron Density Change of 3,5-Dicyanopyridine Skeleton

of the individual transitions showed that the LCI calculations using the both bases present also the corresponding weights of the configuration (Fig. 5). The most important transition of the longest-wave band of all the compounds is 1-2' (HMO-LCI within 59.89–70.65%; SCF-LCI within 61.86–73.11%), except for the compound *III* where the transition 1-1' (58.64%) is the most important, and except for *IV* the

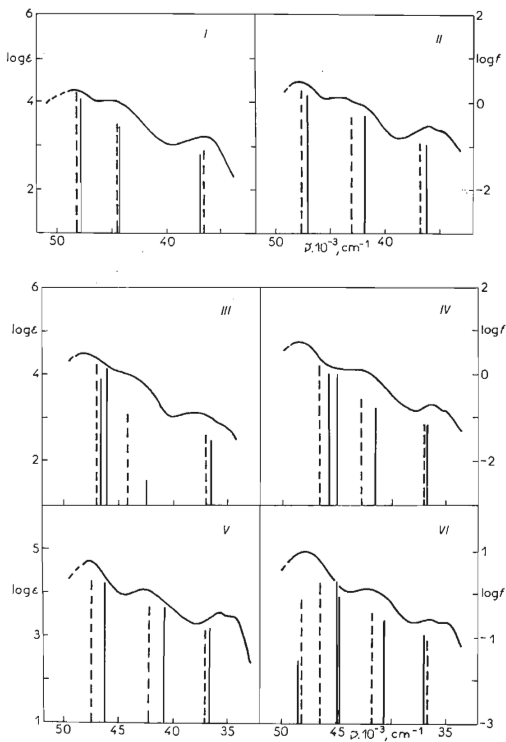


FIG. 4

Experimental UV Spectra of Compounds *I–VI* and their Theoretical Calculation by PPP (—) and HMO-LCI (-----) Methods

FIG. 5  
Comparison of Weights of Configurations for Compound *V* Obtained by the both Procedures (width of arrow represents percentage of configuration in the given transition)

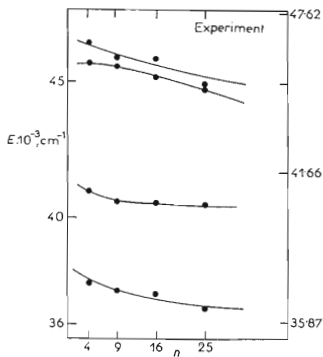
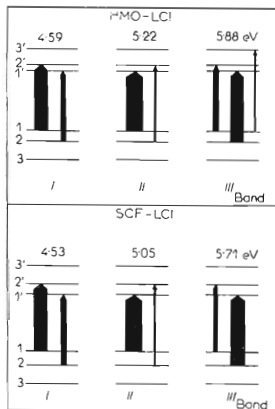


FIG. 6  
Influence of CI Width on Band Position Calculation for Compound *VI* ( $n$  = number of configurations)

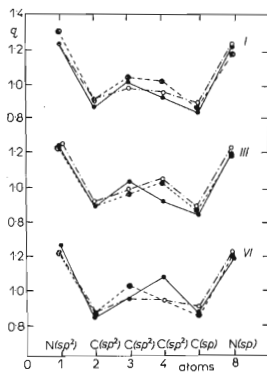


FIG. 7  
Change of  $\pi$ -Electron Density of Compounds *I*, *III*, and *VI* in the Ground and the First Two Excited States (— ground state, ---- the first excited state, - · - · - the second excited state)



last band of which is a mixture of all four energetically lowest configurations. Influence of the quantity of the considered configurations on the quality of interpretation of the spectra has been studied, too. With the changing CI width the photochemically interesting long-wave bands approach in the limit to the value found experimentally (Fig. 6). Number of 16 configurations appears to be sufficient for good interpretation. In the short-wave region the calculated transition does not correspond to experiment, which could probably be improved by a greater CI width and by considering some bi-excited configurations.

Fig. 7 gives typical electron density distribution changes for the first and the second excited states. In the excited states in all cases the  $\pi$ -electron densities are increased at  $\alpha$ - and  $\gamma$ -positions partially to the detriment of  $\beta$ -position, the bond orders being decreased. The electron density at nitrile groups changes but slightly during transition to the excited state whereby the studied heteroaromatic compounds *I* to *VI* differ markedly from analogous heteroolefinic dihydro derivatives<sup>15</sup>.

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