

# ELECTRONIC SPECTRA OF 2- AND 4-SUBSTITUTED 3,5-DICYANO-6-METHYLPYRIDINES

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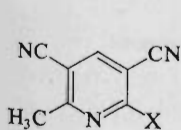
Received November 19th, 1980

The PPP method has been used for calculation of theoretical spectra of the compounds *III*–*X* and *IIIa*–*Xa*, and the results obtained have been confronted with available experimental absorbance curves. It has been shown that the theoretical spectra can be used for successful interpretation of tautomeric equilibrium between 2-pyridone *XI* and 2-hydroxypyridine *X* as well as for prediction of spectral characteristics of the not yet synthesized series *IIIa*–*Xa*.

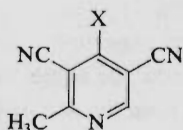
In the course of our studies of optical properties of 3,5-dicyanopyridine derivatives we were interested in the extent to which the LCI method can be used in its  $\pi$  approximation for prognostication of electronic absorption spectra of the compounds *I*–*X* and *IIa*–*Xa*. Whereas some of the 2-substituted derivatives *I*–*VII* have already been described by us<sup>1</sup>, and their real spectra could be measured, the present quantum chemical study should have contributed to decision to synthesize analogous position isomers *IIa*–*Xa*. On the basis of positive results obtained by application of the PPP method to dicyanopyridine series<sup>2,3</sup> we have involved in this study also some not yet synthesized 2-substituted derivatives *VIII*, *IX*, as well as the N-methyl analogue of the compound *XI*.

## EXPERIMENTAL

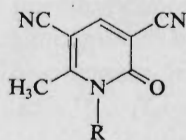
All the used substances described in ref.<sup>1</sup> were purified by sublimation or crystallization. The UV spectra were measured with an Optica Milano apparatus in ethanolic solutions of  $5 \cdot 10^{-4}$  mol l<sup>-1</sup> concentrations at  $30 \pm 1^\circ\text{C}$ .



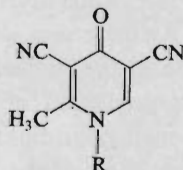
*I*–*X*



*IIa*–*Xa*



*XI*–*XII*



*XIa*–*XIIa*

<i>I</i> , X = H	<i>IV</i> , X = (CH <sub>3</sub> ) <sub>2</sub> N	<i>VII</i> , X = I	<i>X</i> , X = OH
<i>II</i> , X = CH <sub>3</sub>	<i>V</i> , X = Cl	<i>VIII</i> , X = F	<i>XI</i> , R = H
<i>III</i> , X = C <sub>2</sub> H <sub>5</sub> O	<i>VI</i> , X = Br	<i>IX</i> , X = CN	<i>XII</i> , R = CH <sub>3</sub>

#### CALCULATION AND PARAMETERS

The calculations of UV spectra were carried out with an Elliott 503 computer by the MO SCF LCI method in the version by Pople, Pariser and Parr<sup>4,5</sup>. The elements of the **F** matrix were expressed according to Pople, and the coulombic integrals were approximated by the ionisation potential. The ionisation potential values, electron affinities, and resonance integrals are listed in Table I. The following geometry was used: the heteroaromatic ring as regular hexagon with bond angles 120° and bond lengths 0.139 nm. The bicentric repulsion integrals were approximated according to Mataga and Nishimoto<sup>6</sup>. 25 monoexcited configurations were involved in the calculation of configuration interaction. In the calculation the intensity is characterized by logarithm of the oscillator strength. In Table II empirical relation between the oscillator strength and the extinction coefficient is used ( $\log \epsilon = \log f + 4$ ).

#### RESULTS AND DISCUSSION

The experimentally described derivatives *III*–*VII* (X = Cl, Br, I, C<sub>2</sub>H<sub>5</sub>O and (CH<sub>3</sub>)<sub>2</sub>N) exhibit UV spectra characteristic of aromatic substituted derivatives of pyridine or benzene type<sup>7</sup> (Table II). Position of the longest-wave band is sensitive to variation of substituent at 2 position. The electron-acceptor substituents (X = Cl, Br, I) cause a hypsochromic shift of this band, whereas the electron-donor substituents (X = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>O, (CH<sub>3</sub>)<sub>2</sub>N) have an opposite effect. An anomalous behaviour is observed with 2-iodo-3,5-dicyano-6-methylpyridine (*VII*) where substantial intensity increase of the longest-wave band is explained by the  $n-\pi^*$  transition of iodine atom. The second absorption band ( $\lambda_{\max} = 244-249$  nm) is little sensitive to change of the substituents, and its intensity is nearly constant ( $\log \epsilon = 4.03-4.11$ ).

An exception from this group forms 2-dimethylamino-3,5-dicyano-6-methylpyridine (*IV*) showing a considerable bathochromic effect of the both longest-wave  $\pi-\pi^*$  transitions ( $\Delta 45$  nm), which is analogous to the case of benzene and dimethylaniline and typical of aromatic compounds carrying dimethylamino group<sup>8</sup>.

In the theoretically calculated spectra the longest-wave band always represents a superposition of the 1→1' and 1→2' transitions for the electron-acceptor substituents, whereas for the electron-donor substituents the transition 1→1' predominates in this band (weight of configuration above 50%).

As there was a very good agreement between experiment and theoretical calculation in the studied series of compounds, we used the same calculation parameters for prediction of optical properties of the isomeric 4-X-substituted 3,5-dicyano-6-methylpyridines (*IIIa*–*Xa*). The calculated spectra of this series differ but little from those of the 2-substituted derivatives. The longest-wave band represents a superposition of two types of transition (1→2' and 2→1'), the configuration 1→2' being

preferred (about 60% of weight). This fact applies first of all to the 4-halogeno-substituted derivatives *Va*–*VIIIa*. For the compounds *IVa* and *IXa* the dominant transition types in this band are 1–1' (over 75%).

The second absorption band (calculated  $\lambda_{\max} = 242$  nm) is insensitive to variation of the halogen substituent and does not change until under the influence of an electron-donor substituent ( $X = (\text{CH}_3)_2\text{N}$ ,  $\text{C}_2\text{H}_5\text{O}$ ). The calculated spectra of the series *IIIa*–*Xa* are given in Table III.

*Electron distribution.* The charge distribution of  $\pi$  electrons in the studied series resembles considerably that of the methyl substituted 3,5-dicyanopyridines<sup>2</sup>. Introduction of a substituent into the 2 or 4 position does not markedly influence the electron distribution of the 3,5-dicyanopyridine skeleton. Depending on the substituent type, a certain change takes place in its near surroundings only. The electron density change at the pyridine nitrogen atom agrees quantitatively with conjugation effect of the substituent which is always located at *ortho* or *para* position of the pyridine nucleus in the series studied. The most marked change of distribution of the  $\pi$  electron skeleton is caused by introduction of dimethylamino group, the bond order of which being in the both cases (2 and 4 positions) close to the character of double

TABLE I  
SCF calculation parameters (for zero iteration in all the SCF calculations  $h_X = 0$ )

Atom	<i>I</i> eV	<i>A</i> eV	Bond	<i>k</i> <sub>CX</sub>	<i>Z</i>	<i>r</i> <sub>CX</sub> nm
C( <i>sp</i> <sup>2</sup> )	11.16	0.03	C( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>2</sup> )	1.0	1	0.139
N( <i>sp</i> <sup>2</sup> )	14.12	1.78	N( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>2</sup> )	1.0	1	0.139
C( <i>sp</i> )	11.19	0.10	C( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> )	0.9	1	0.146
N( <i>sp</i> )	14.18	1.66	C( <i>sp</i> )—N( <i>sp</i> )	1.4	1	0.116
C( <i>sp</i> <sup>3</sup> )	11.42	0.58	C( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>3</sup> )	0.51	1	0.152
H <sub>3</sub> ≡C	9.50	0.0	H <sub>3</sub> —C	1.25	1	0.110
CH <sub>3</sub> O <sup>a</sup>	33.00	11.47	CH <sub>3</sub> O—C( <i>sp</i> <sup>2</sup> )	0.78	2	0.137
NH (pyrrole)	24.80	8.04	N( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>2</sup> )	0.78	2	0.138
NH (pyridone)	29.16	14.49	N( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>2</sup> )	0.8	2	0.139
O=C( <i>sp</i> <sup>2</sup> )	17.28	2.7	O( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>2</sup> )	1.6	1	0.124
O—H( <i>sp</i> <sup>2</sup> )	30.46	10.16	O( <i>sp</i> <sup>2</sup> )—C( <i>sp</i> <sup>2</sup> )	0.78	2	0.136
Cl	28.67	15.09	Cl—C( <i>sp</i> <sup>2</sup> )	0.70	2	0.169
Br	24.60	13.72	Br—C( <i>sp</i> <sup>2</sup> )	0.65	2	0.186
I	21.00	12.61	I—C( <i>sp</i> <sup>2</sup> )	0.1	2	0.202
F	43.07	20.98	F—C( <i>sp</i> <sup>2</sup> )	1.0	2	0.130
(CH <sub>3</sub> ) <sub>2</sub> N <sup>a</sup>	24.30	7.54	(CH <sub>3</sub> ) <sub>2</sub> N—C( <i>sp</i> <sup>2</sup> )	1.0	2	0.136

<sup>a</sup> Heteroatomic model.

TABLE II  
Comparison of calculated and experimental spectral characteristics of compounds III—X

Compound	$E \cdot 10^{-3}$ $\text{cm}^{-1}$	SCF LCI			Experiment	
		$\log f + 4$	$i - j$	%	$E \cdot 10^{-3} \text{ cm}^{-1}$	$\log \epsilon$
III <sup>a</sup>	34.19	3.27	1-1'	54.59	33.56	3.83
	39.69	3.62	1-2'	57.34	40.32	4.11
			1-1'	31.28		
	45.39	4.18	2-1'	32.54	46.73	4.40
			2-2'	28.13		
IV	29.26	3.42	1-1'	89.95	29.15	3.67
	26.65	3.78	1-2'	88.68	34.48	4.35
	41.97	3.43	1-3'	71.37		
	45.52	4.01	2-1'	72.84	46.73	4.18
	35.78	3.10	1-2'	42.07	35.21	3.52
		1-1'	28.96			
V	40.40	3.63	1-1'	59.37	40.98	4.07
			1-2'	27.40		
	46.09	4.15	2-1'	39.86	46.73	4.44
VI	35.37	3.12	1-2'	40.41	34.96	3.51
			1-1'	30.35		
	40.94	3.64	1-1'	56.48	40.16	4.05
		1-2'	31.60			
VII	46.22	4.18	2-1'	37.97	46.04	4.40
	35.92	3.00	1-2'	61.89	36.10	3.86
	41.40	3.66	1-1'	83.47	40.82	4.03
	46.55	4.17	2-1'	49.63	46.51	4.48
		1-2'	26.74			
VIII <sup>b</sup>	35.37	3.13	1-1'	35.00	—	—
			1-2'	34.90		
	41.20	3.64	1-1'	51.13		
			1-2'	36.18	—	—
	4.17	2-1'	31.96			
		2-2'	26.66	—	—	
IX <sup>b</sup>	35.22	3.20	1-2'	36.87	—	—
			1-1'	35.72		
	39.34	3.64	1-1'	54.55	—	—
			1-2'	33.18		
	4.25	2-1'	58.36	—	—	
		1-2'	25.07			
X <sup>c</sup>	34.51	3.39	1-1'	71.80	29.94	3.94
	39.28	4.63	1-2'	71.70	36.76	4.31
	45.28	4.05	2-1'	50.26	47.62	4.28
			2-2'	28.68		

bond ( $p_{ij} = 0.57$ ). Effect of this group makes itself felt also in change of  $\pi$  electron distribution and bond order of the cyano groups (see ref.<sup>2</sup>) (Fig. 1).

The situation in the first and the second excited states  $S_1$  and  $S_2$  was approximated by the configurations 1' and 2' in accordance with data of Table II. It was found that changes of  $\pi$  electron distribution were similar for all the investigated derivatives of the series  $I-X$  except for the derivative  $IV$ . From Fig. 2 it is seen that in the whole series the  $S_1$  state is characterized by increased electron density at the  $C_{(4)}$  and  $N_{(1)}$  atoms and, furthermore, by considerable weakening of  $\pi$  delocalization in the pyridine nucleus. In the  $S_2$  state the most marked weakening of the  $\pi$  bond character is within the groupings  $C_{(2)}-C_{(3)}-C_{(4)}$  (the bond order  $p_{23} = 0.375$ ) and  $C_{(5)}-C_{(6)}-N_{(1)}$  ( $p_{56} = 0.342$  for the derivative  $V$ ). The most marked increase in the  $\pi$  electron density is at the 6 and 2 positions. Cyano-groups are relatively insensitive to variation of electron density in  $S_1$  and  $S_2$  except for the derivative  $IV$ , where there is a certain increase at the CN bond to  $C_{(3)}$  (in  $S_1$ ) and at  $NC-C_{(5)}$  (in  $S_2$ ). Similar facts are also observed in the series  $Ia-Xa$ . On the whole it can be stated that the electron distribution of the excited states  $S_1$  and  $S_2$  differs only little from that of the  $S_0$  state.

*Pyridine-pyridone tautomerism*  $X \rightleftharpoons XI$ . On the basis of IR spectrum, which exhibits a characteristic carbonyl vibration  $\nu_{C=O} = 1670 \text{ cm}^{-1}$ , and position of the longest-wave band in UV spectrum ( $\lambda_{\text{max}} = 334 \text{ nm}$ ,  $\log \epsilon = 3.94$ ) it can be suggested that  $XI$  represents 2-pyridone tautomer, or this form considerably predominates. We tried to confirm this suggestion also by application of the PPP method to interpretation of the calculated UV spectrum of the compound  $XI$  and its hydroxyl analogue  $X$ . These derivatives should have UV spectra similar to those of their alkylated analogues  $XII$  and  $III$ .

UV spectrum of 1,2-dimethyl-3,5-dicyano-6-pyridone ( $XII$ ) is characterized by three absorption bands in the regions 220 nm ( $\log \epsilon = 4.24$ ), 255 nm ( $\log \epsilon = 4.2$ ) and 340 nm ( $\log \epsilon = 4.02$ ). In contrast to this spectrum the absorption curve of 2-ethoxy-3,5-dicyano-6-methylpyridine ( $III$ ) exhibits a typical aromatic band in the region 248 nm ( $\log \epsilon = 4.11$ ) and a considerably hypsochromically shifted longest-wave band with a lower extinction coefficient ( $\lambda_{\text{max}} = 298 \text{ nm}$ ,  $\log \epsilon = 3.83$ ). The experimental spectrum of the compound  $XI$  resembles (by its shape and values of the extinction coefficients) that of the N-substituted pyridone model  $XII$ , which confirms the existence of this compound in the form of the pyridone isomer. Calculation of the spectra by the PPP method also confirms these conclusions (Fig. 3). The longest-wave band of the compound  $XI$  is predicted at 324 nm, which represents a 10nm difference from experiment. The analogous band of the compound  $X$  is predicted

<sup>a</sup> The calculation carried out for 2-methoxy-3,5-dicyano-6-methylpyridine; <sup>b</sup> the compounds not synthesized so far; <sup>c</sup> the experimental UV data for 3,5-dicyano-6-methyl-2-pyridone.

TABLE III  
The calculated UV spectra of the compounds IIIa—Xa

Compound	$E \cdot 10^{-3} \text{ cm}^{-1}$	$\log f + 4$	$i - j$	%
IIIa	35.03	3.89	2-1'	47.57
			1-2'	45.31
	40.30	3.32	1-1'	72.58
	43.52	3.14	1-2'	43.29
			2-1'	41.04
IVa	45.60	3.83	2-2'	57.05
	29.87	3.26	1-1'	89.48
	37.30	2.50	1-2'	74.21
	41.30	3.89	2-2'	78.66
	42.90	3.77	2-1'	64.16
Va	44.04	3.78	1-3'	78.19
	35.68	2.68	1-2'	59.84
			2-1'	32.12
	41.26	3.61	1-1'	86.36
	45.72	4.18	2-1'	52.30
VIa			1-2'	33.44
	35.68	2.67	1-2'	59.39
			2-1'	32.63
	41.19	3.59	1-1'	85.46
	45.56	4.18	2-1'	51.95
VIIa			1-2'	33.63
	35.92	2.99	1-2'	62.07
	41.39	3.66	1-1'	83.78
	46.51	4.17	2-1'	49.90
			1-2'	26.98
VIIIa	35.77	2.65	1-2'	59.80
			2-1'	32.34
	41.28	3.64	1-1'	87.47
	45.88	4.18	2-1'	52.69
			1-2'	33.84
IXa	34.42	3.22	1-1'	76.30
	40.51	2.90	1-2'	60.62
			2-1'	36.60
	44.38	4.08	2-1'	49.95
	45.25	4.01	2-2'	56.14
Xa	34.18	2.06	1-1'	40.30
			2-2'	25.20
	39.40	2.73	1-2'	41.71
			2-1'	36.22
	42.24	4.09	2-2'	59.67
		1-1'	31.00	
	43.95	3.92	2-1'	42.65
			1-2'	39.03

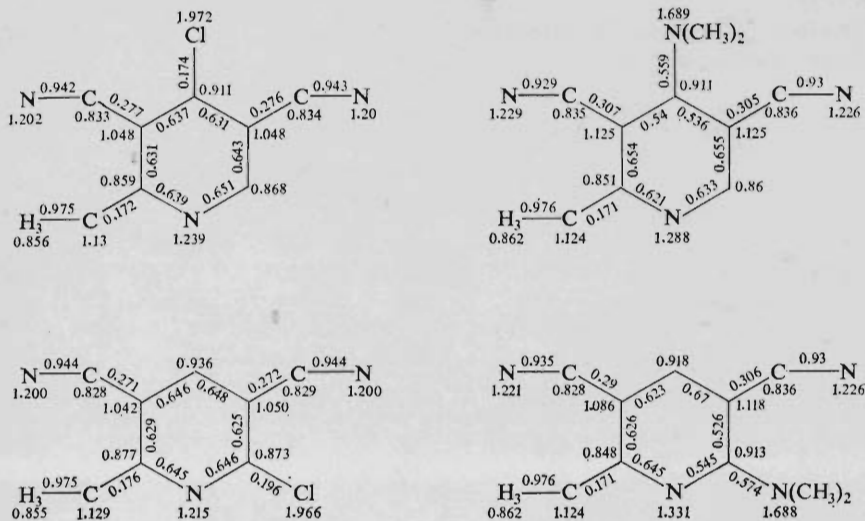


FIG. 1  
Molecular diagram of compounds *IV*, *IVa*, *V*, and *Va* in  $S_0$  state

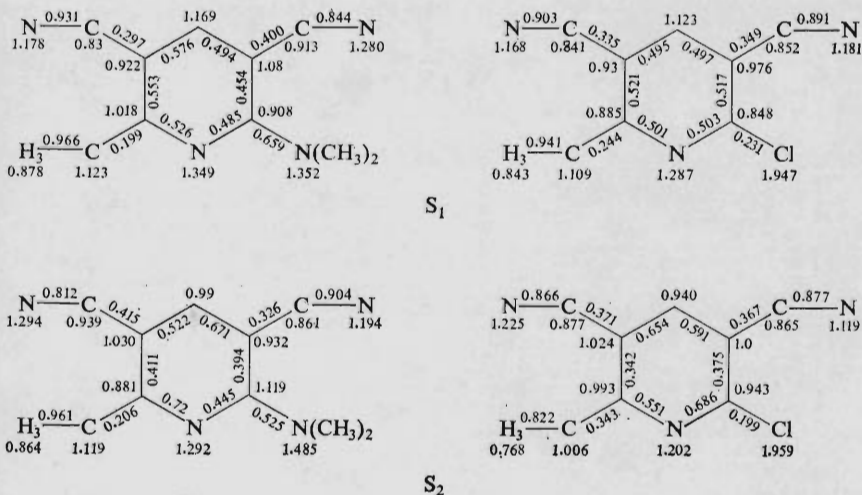


FIG. 2  
Molecular diagram of compounds *IV* and *V* in their  $S_1$  and  $S_2$  states



TABLE IV

The calculated UV spectra of the substituted  $\alpha$ - and  $\gamma$ -pyridones. The compounds *XIa* and *XIIa* have not been synthesized yet

Compound	$E \cdot 10^{-3}$ $\text{cm}^{-1}$	SCF LCI			Experiment	
		$\log f + 4$	$i - j$	%	$E \cdot 10^{-3}$ $\text{cm}^{-1}$	$\log \epsilon$
<i>XI</i>	30.87	3.86	1-1'	97.00	29.94	3.94
	39.33	3.30	1-2'	81.08	36.76	4.31
	43.57	3.37	2-1'	78.82	—	—
	48.31	3.10	1-3'	75.80	47.62	4.28
<i>XII</i>	30.76	3.85	1-1'	97.62	29.41	4.02
	39.86	3.36	1-2'	82.82	39.22	4.20
	42.86	2.61	2-1'	78.42	—	—
	44.10	3.55	3-1'	66.25	45.45	4.24
<i>XIa</i>	37.46	3.46	1-1'	58.29	—	—
			1-2'	31.17		
	38.02	3.34	1-2'	65.79	—	—
	40.20	2.93	1-1'	27.04	—	—
			2-1'	83.62		
46.03	3.89	2-2'	56.17	—	—	
<i>XIIa</i>	37.52	3.37	1-2'	59.57	—	—
			1-1'	34.25		
	37.89	3.50	1-1'	52.03	—	—
			1-2'	38.26		
	40.28	2.96	2-1'	85.67	—	—
45.94	3.96	2-2'	59.70	—	—	

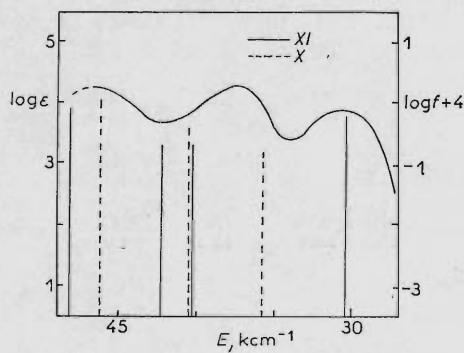


FIG. 3  
PPP calculation of UV spectra of isomers *X* and *XI*



at 289.7 nm. There is also a considerable difference between total  $\pi$  electron energies of the studied compounds, the calculated values for the derivatives *X* and *XI* being  $-205.57$  and  $-212.03$  eV, respectively.

Using the same parameters we also calculated UV spectra of the substituted 4-pyridone *XIa* and its hydroxyl tautomer *Xa* and compared them with those of the N- and O-alkylated derivatives *IIIa* and *XIIa*. The calculated data are summarized in Table IV. The substituted 4-pyridone *XIa* should have its longest-wave band at 267 nm, which also confirms the preferred formation of the 2-isomer *XI* in the cyclocondensation reaction of ethyl alkoxymethylenecyanoacetate with 3-amino-crotonitrile, as it was found in ref.<sup>1</sup>.

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Translated by J. Panchartek.