

ELECTRONIC STRUCTURE AND SPECTRA OF ORGANIC MOLECULES. PART XV^{1,2}. SCF MO CI CALCULATIONS FOR NEUTRAL, CATIONIC AND ANIONIC FORMS OF DIOXOPYRIDINES

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The Pariser-Parr-Pople type of calculations were carried out for thirty four forms (neutral, cationic and anionic) of dioxosubstituted pyridines. The calculated spectra (singlet-singlet transitions, $\pi \rightarrow \pi^*$ type) agree well with experimental measurements.

Introduction

Systematic attempts have been made in our previous papers (Berndt and Kwiatkowski 1970, Kwiatkowski 1970, 1971a, b, Kwiatkowski and Olzacka 1970, Kwiatkowski *et al.* 1970) to interpret the π -electronic structures and spectra of both neutral and ionic (anionic and cationic) forms of pyridines and pyrimidines containing substituents being potentially tautomeric groups, such as hydroxy, amino or mercapto ones. The interesting features of the π -spectra of the molecules were interpreted on the basis of the theoretical results obtained by means of the semiempirical SCF MO CI method (PPP method). It is the purpose of the present paper to extend the same type of calculations to neutral, anionic and cationic (protonated) forms of dioxosubstituted pyridines. Since the details of computational procedure and the choice of the semiempirical parameters are the same as those in the papers mentioned above, we will only comment on the assumed electronic structures of the molecules under consideration (see below).

Results of calculations. Discussion

Electronic structures of neutral monooxosubstituted pyridines may be unambiguously determined (comp. Kwiatkowski 1971b). However, the determination of the structures of dioxopyridines is more difficult because of the small number of appropriate experimental

¹ For Part XIV ("On the Lactam and Thione Forms of Pyridines and Pyrimidines") see Kwiatkowski, J. S., *J. Molec. Structure*, in press.

² The paper was begun in a collaboration with Miss B. Kamińska.

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data. Therefore, the assumption is made that the structures of monooxosubstituted pyridines are not changed when the molecule is substituted by the second hydroxy (or methoxy) group. Thus, all the dioxosubstituted molecules, except 3,5-dioxypyridine having the lactim structure (VI), exist as the lactams (Ia, IIa, IIb, IIIa, IVa, Va). It should be noted that Spinner

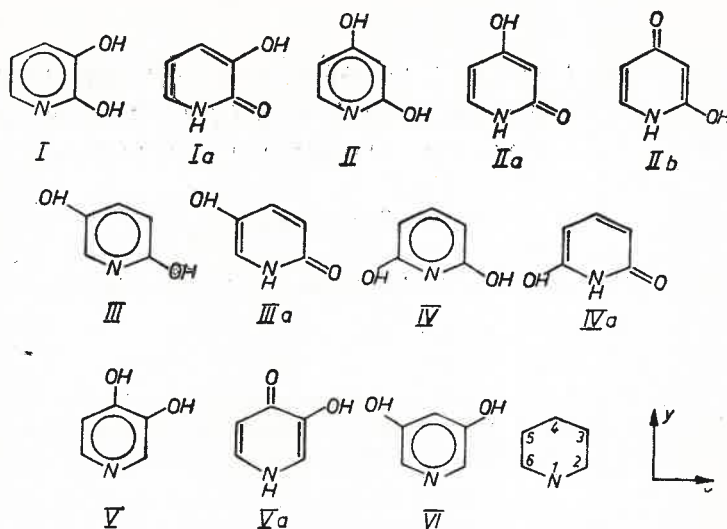


Fig. 1. Numbering of atoms in pyridines. The polarization direction (angle Θ) is measured counterclockwise from the line C_6-C_2 (the x axis).

Dioxypyridines under study:

Neutral forms:

- 2,3-dioxypyridine: I 2,3-diOH-pyridine (lactim),
Ia 3-OH-2-pyridone (lactam).
- 2,4-dioxypyridine: II 2,4-diOH-pyridine (lactim),
IIa 4-OH-2-pyridone (lactam),
IIb 2-OH-4-pyridone (lactam).
- 2,5-dioxypyridine: III 2,5-diOH-pyridine (lactim),
IIIa 5-OH-2-pyridone (lactam).
- 2,6-dioxypyridine: IV 2,6-diOH-pyridine (lactim),
IVa 6-OH-2-pyridone (lactam).
- 3,4-dioxypyridine: V 3,4-diOH-pyridine (lactim),
Va 3-OH-4-pyridone (lactam).
- 3,5-dioxypyridine: VI 3,5-diOH-pyridine (lactim).

Cationic and anionic forms — for the structures of cations and anions of dioxypyridines see text

and White (1966a, b) have investigated the effect of the substituents CH_3 , OCH_3 , OH , O^- , Cl , Br and NO_2 on the structure of 2-oxypyridine. A comparison of the ultraviolet spectra of these derivatives of 2-oxypyridine with the corresponding derivatives of 2-methoxypyridine indicates that the former ones have the lactam structure. This conclusion has been confirmed by a study the infrared spectra (Spinner and White 1966a, b).

For a comparison the PPP calculations were carried out for the lactim structures of

TABLE I

Neutral forms of dioxopyridines — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths¹, f , logarithms of molar extinction coefficients¹, $\log \epsilon$, and polarization direction, Θ (in degrees)

Lactim structures			Lactam structures			
Theoretical		Experimental	Theoretical		Experimental	
$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$	$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$	
2,3-Dioxopyridine						
(I)			(Ia)			
4.442(0.129)	-5	4.43(3.76) ^{2,3}	4.374(0.372)	7	4.17(3.87) ²	4.20(3.8) ⁴
5.575(0.138)	76	5.61(3.76)	5.225(0.171)	-78	5.30(3.61)	5.39(3.8)
6.603(0.906)	-54		6.194(0.304)	-53		5.41(3.91) ⁷
6.704(0.944)	32		6.893(0.310)	-18		5.32(3.67)
2,4-Dioxopyridine						
(II)			(IIa)			
4.604(0.042)	20	4.77 ^{5,8} 4.77(3.3) ^{8,10}	4.465(0.246)	9	4.49(3.65) ^{5,11}	4.43(36.6) ^{8,6}
5.709(0.015)	27	5.64 5.57 sh (3.6)	5.397(0.069)	-49		4.44(3.6) ^{5,18}
6.396(1.175)	-54		1.47(0.874)	-59		
6.552(0.888)	42		6.748(0.240)	1		
			(IIb)			
			4.781(0.480)	-76	5.00(4.05) ^{5,13}	4.94(4.05) ^{5,14}
			4.989(0.075)	65		
			5.667(0.236)	19		
			6.993(1.021)	-81		
2,5-Dioxopyridine						
(III)			(IIIa)			
4.395(0.131)	26		4.203(0.269)	19	3.87(3.75) ⁷	3.86(3.7) ¹⁵
5.606(0.255)	-43		5.451(0.211)	-52	5.38(3.87)	5.28(3.8)
6.685(0.946)	-54		6.469(0.794)	-46		
6.869(0.845)	33		6.698(0.011)	-35		
2,6-Dioxopyridine						
(IV)			(IVa)			
4.485(0.134)	0	4.48(3.7) ^{4,16} 4.44-4.46(3.8) ^{10,17}	4.304(0.353)	12	4.05(3.89) ²	3.87(4.2) ⁴
5.730(0.159)	90	5.71(3.7) 5.51-5.56(4.0)	5.554(0.244)	-64	5.51(3.83)	5.28(3.8) 5.22(3.9)
6.720(1.045)	0		6.572(0.091)	-24		
6.781(0.895)	90		6.787(0.506)	-57		
3,4-Dioxopyridine						
(V)			(Va)			
4.555(0.041)	-43		4.491(0.429)	-74	4.51(4.1) ⁴	4.46(4.31) ^{6,9}
5.502(0.086)	-26		4.887(0.131)	53	4.54(4.0) ⁷	4.41(4.1) ¹⁹
6.382(1.106)	47		5.660(0.226)	33	5.77(4.5)	
6.555(0.851)	-49		7.024(0.719)	82		

TABLE I (continued)

Lactim structures			Lactam structures			
Theoretical		Experimental	Theoretical		Experimental	
$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$	$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$	

3,5-Dioxypyridine

(VI)

4.455(0.099)	0	4.43(3.8) ⁴
5.598(0.049)	90	5.64(3.9)
6.459(0.843)	90	
6.493(1.062)	0	

sh = shoulder

¹ The f - and $\log \epsilon$ -values are given in parenthesis.² Spinner and White (1966a).³ Data for 2-methyl-3-oxopyridine.⁴ den Hertog *et al.* (1950).⁵ den Hertog and Burman (1956).⁶ Data for 1-methyl derivative.⁷ Behrman and Pitt (1958).⁸ Data for 2,4-dimethoxypyridine.⁹ Adams *et al.* (1947).¹⁰ Favini *et al.* (1968).¹¹ Data for 4-methoxy-2-pyridone.¹² Data for 4-methoxy-1-methyl-2-pyridone.¹³ Data for 2-methoxy-4-pyridone.¹⁴ Data for 2-methoxy-1-methyl-4-pyridone.¹⁵ Behrman and Stanier (1957).¹⁶ Data for 2,6-dioxyppyridine.¹⁷ Data for 2,6-dimethoxypyridine.¹⁸ Ames *et al.* (1953). Absorption bands of 1,4-dimethyl derivative of the molecule have two maxima (ΔE in eV, $\log \epsilon$): 4.11 (3.83), 5.44 (3.89).¹⁹ Berson *et al.* (1956).

dioxypyridines (I-V) existing in the lactam forms. In these cases the experimental data for corresponding methoxy derivatives of pyridine were treated as references. Comparison of this kind may be made because the replacement of a hydrogen atom by a methyl group in the -OH substituent makes only a slight change in the spectrum.

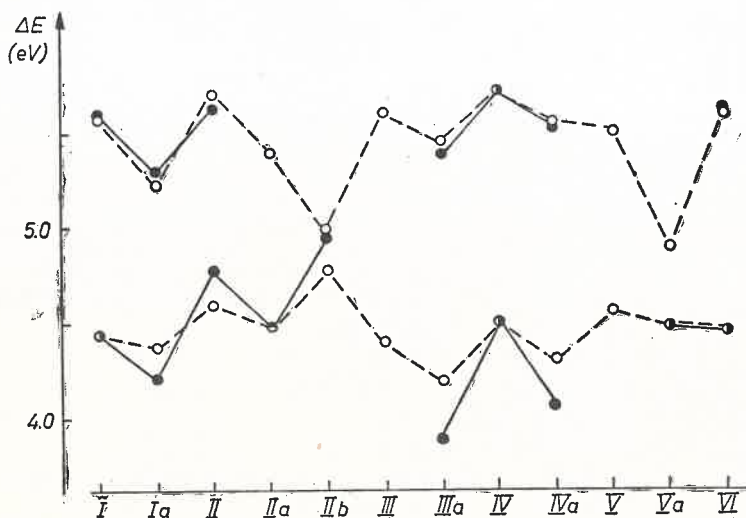


Fig. 2. Comparison between observed (●) and calculated (○) singlet-singlet transition energies for dioxosubstituted pyridines. Actual data and numbering of the molecules are in Table I and Fig. 1

TABLE II

Protonated dioxypyridines — singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f , logarithms of molar extinction coefficients, $\log \epsilon$, and transition polarizations, Θ (in degrees)

Theoretical			Experimental		
ΔE	f	Θ	$\Delta E(\log \epsilon)$		
2,3-Dioxypyridine					
4.229	0.268	-10	4.28(3.92) ¹	4.20(3.91) ²	4.20(3.8) ³
5.368	0.057	53	5.58(3.45)	5.32(3.67)	5.39(3.6)
6.296	0.845	85			
6.747	0.693	-3			
2,4-Dioxypyridine					
4.486	0.174	-1	4.51(3.5) ³		
5.375	0.075	-87	~5.64(3.3)		
6.266	1.084	-69			
6.438	0.600	28			
2,5-Dioxypyridine					
4.203	0.248	12	4.04(3.70) ²	3.94(3.6) ³	
5.429	0.087	-43	5.53(3.79)		
6.238	0.934	-62			
6.858	0.581	25			
2,6-Dioxypyridine					
4.197	0.307	0	4.25(4.05) ¹	4.20(3.8) ³	4.26(3.84) ⁴
5.582	0.142	90	5.71(3.68)	5.64(3.7)	5.94(3.88)
6.558	0.911	90			
6.913	0.609	0			
3,4-Dioxypyridine					
4.500	0.140	-29	4.63(3.71) ²	4.51(3.6) ³	
5.086	0.096	-69	5.14(3.54)	5.28(3.5)	
6.172	0.998	42			
6.594	0.722	-61			
3,5-Dioxypyridine					
4.334	0.190	0	4.43(3.9) ³		
5.211	0.011	90	5.39(3.8)		
6.200	0.800	90			
6.405	0.887	0			

¹ Spinner and White (1966b). Absorption bands of 2-methoxy-3-oxypyridine have two maxima (ΔE in eV, $\log \epsilon$): 4.25(3.92), 5.41(3.60).

² In 0.1N HCl, Behrman and Pitt (1958).

³ In 0.1N HCl, den Hertog *et al.* (1950).

⁴ In 0.1N HCl, Ames *et al.* (1953).

As to the structures of the anions of the molecules under study, we assumed analogously as in our previous paper (Berndt and Kwiatkowski 1970) that the negative charge is concentrated on the oxygen atom $-O^-$. The calculations were done for all sixteen mono-anions and dianion of 2,6-dioxypyridine. In the cases of protonated molecules the calculations were performed in the same way as in our previous paper (Kwiatkowski 1971a), *i. e.* it was assumed that the proton was attached to the pyridinic nitrogen, and the same parameters corresponding to the previous electrostatic model were used.

(a) Neutral dioxypyridines

Table I contains the results of the PPP calculations for all neutral forms of dioxypyridines. The results are compared with the experimental data.

It is evident that the calculated ΔE values are in a good agreement with the experimental ones. Generally, the greatest differences between the theoretical and experimental transi-

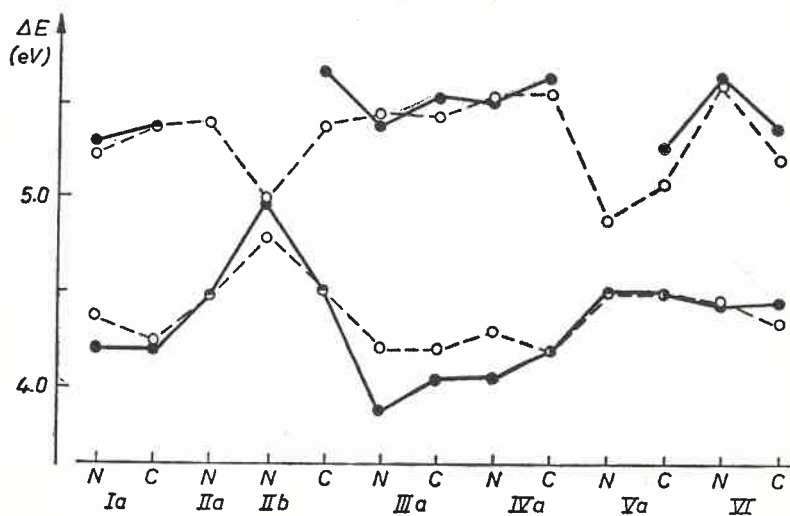


Fig. 3. Comparison between observed (●) and calculated (○) singlet-singlet transition energies for neutral (N) and protonated (C — cations) dioxypyridines. Actual data and numbering of the molecules are given in Tables I, II and Fig. 1

tion energies are of the order of 0.2–0.25 eV (except for the first transition energy for the lactam form of 2,5-dioxypyridine, where it is of the order of 0.3 eV). A comparison between experimental and theoretical data is better illustrated in Fig. 2. From the figures presented in Table I it can be seen that the lactam forms of the molecules absorb at a longer wavelengths region than the lactim forms.

(b) Protonated dioxypyridines

The calculation results correctly interpret the observed shifts of the absorption bands of the pyridines when protonation occurs (Fig. 3). In all the cases of the protonated molecules the differences between the experimental and calculated ΔE -values are not higher than 0.2 eV.

TABLE III

Anionic forms of dioxopyridines — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths¹, f , logarithms of molar extinction coefficients¹, $\log \epsilon$, and transition polarization, Θ (in degrees)

Lactim structures			Lactam structures		
Theoretical		Experimental	Theoretical		Experimental
$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$	$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$
2,3-Dioxopyridine monoanions					
2-O ⁻ -3-OH-pyridine					
4.236(0.164)	2	[4.17] ²			
5.259(0.234)	-73	[5.25]			
6.381(0.590)	15				
6.424(0.679)	-57				
2-OH-3-O ⁻ -pyridine			3-O ⁻ -2-pyridone		
4.176(0.152)	-16	4.19(3.83) ^{3,4} [4.22] ²	4.146(0.409)	2	4.0(3.96) ³ 4.0(3.9) ^{5,6}
5.160(0.257)	51	5.12(3.95) [5.12]	4.838(0.195)	75	4.86
6.168(0.432)	-79		5.632(0.080)	-85	
6.533(0.876)	10		6.659(0.313)	-19	
2,4-Dioxopyridine monoanions					
2-O ⁻ -4-OH-pyridine			2-O ⁻ -4-pyridone		
4.386(0.075)	23		4.607(0.445)	-66	
5.439(0.184)	-39		4.927(0.018)	-86	
6.148(0.924)	-48		5.447(0.309)	36	
6.306(0.572)	54		6.402(0.934)	-75	
2-OH-4-O ⁻ -pyridine			4-O ⁻ -2-pyridone		
4.505(0.011)	39	} [4.5-4.9] ² [5.8]	4.404(0.231)	-6	
5.323(0.228)	-89		5.057(0.013)	40	
6.027(0.670)	-6		5.701(0.915)	-73	
6.192(0.915)	-86		6.276(0.330)	-9	
2,5-Dioxopyridine monoanions					
2-O ⁻ -5-OH-pyridine					
4.149(0.154)	27				
5.311(0.416)	-43				
6.479(0.264)	-11				
6.613(0.615)	-69				
2-OH-5-O ⁻ -pyridine			5-O ⁻ -2-pyridone		
4.086(0.145)	33	[3.99] ²	3.865(0.210)	26	
5.219(0.402)	-37	[5.30]	5.219(0.205)	-55	
6.236(0.348)	-67		5.789(0.660)	-37	
6.680(0.639)	-2		6.604(0.088)	-51	

TABLE III (continued)

Lactim structures			Lactam structures		
Theoretical		Experimental	Theoretical		Experimental
$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$	$\Delta E(f)$	Θ	$\Delta E(\log \epsilon)$
2,6-Dioxypyridine monoanions					
2-OH-6-O ⁻ -pyridine			6-O ⁻ -2-pyridone		
4.291(0.161)	6		4.132(0.414)	12	3.85(4.17) ³
5.444(0.291)	-62		5.471(0.270)	-76	5.30(3.92)
6.402(0.347)	60		6.154(0.073)	50	
6.485(0.818)	-17		6.717(0.468)	-56	
3,4-Dioxypyridine monoanions					
3-O ⁻ -4-OH-pyridine			3-O ⁻ -4-pyridone		
4.251(0.082)	-51		3.954(0.288)	-67	4.01(3.99) ^{5,6}
5.097(0.204)	9		4.649(0.108)	36	
6.086(0.836)	65		5.449(0.382)	56	
6.380(0.577)	-8		6.446(0.494)	63	
3-OH-4-O ⁻ -pyridine					
4.433(0.027)	-80				
5.103(0.220)	-64				
5.972(0.763)	26				
6.336(0.836)	-81				
3,5-Dioxypyridine monoanion					
3-O ⁻ -5-OH-pyridine					
4.220(0.114)	-14				
5.254(0.164)	41				
5.977(0.557)	68				
6.238(0.860)	-10				

¹ The f - and $\log \epsilon$ -values are given in parenthesis.

² Data for the compound, in which the $-O^-$ and $-OH$ substituents are replaced by the $-NH_2$ and $-OCH_3$ groups respectively. For the explanation see text. For experimental data see Favini *et al.* (1968).

³ Spinner and White (1966a).

⁴ Data for anion of 2-methoxy-3-oxypyridine.

⁵ Berson *et al.* (1956).

⁶ Data for 1-methyl derivative.

(c) Anions of dioxypyridines

Unfortunately, the experimental transition energies are only known in a few cases for the anions of the molecules in question. It is evident from Table III that the calculation results do agree with the experimental data wherever the latter are known.

TABLE IV

Neutral, monoanion and dianion of 2,6-dioxypyridine — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f , logarithms of molar extinction coefficients, $\log \epsilon$, and transition polarizations, Θ (in degrees)

Theoretical			Experimental ¹
ΔE	f	Θ	$\Delta E(\log \epsilon)$
2,6-Dioxypyridine (6-OH-2-pyridone)			
4.30	0.353	12	4.05(3.89)
5.55	0.244	-64	5.51(3.83)
6.57	0.091	-24	
6.79	0.506	-57	
2,6-Dioxypyridine monoanion (6-O ⁻ -2-pyridone)			
4.13	0.414	12	3.85(4.17)
5.47	0.270	-76	5.30(3.92)
6.15	0.073	50	
6.72	0.408	-56	
2,6-Dioxypyridine dianion (2,6-diO ⁻ -pyridine)			
4.17	0.188	0	4.03(3.93)
5.32	0.274	90	5.12(3.88)
6.03	0.167	90	
6.11	0.870	0	

¹ Experimental data taken from Spinner and White (1966a, b).
Comp. Table I.

In Table III, for a comparison between the theoretical and experimental results in the case of 2-O⁻-3-OH⁻, 2-OH-3-O⁻, 2-OH-4-O⁻ and 2-OH-5-O⁻-pyridines, we listed the experimental transition energies for pyridine substituted by the methoxy group instead of the hydroxy one and by the amino group instead of the —O⁻ substituent. It is known from spectroscopic evidence that the —O⁻ substituent has slightly stronger electron donor properties with respect to the amino group. Therefore it may be assumed that the replacement of the —O⁻ substituent by the amino group one makes only slight changes (of the order up to 0.1 eV) in a spectrum of a molecule (comp. Berndt and Kwiatkowski 1970).

The figures presented in Table III show that there is better agreement between the calculation results and the experimental data for 3-O⁻-2-pyridone than in the case of 2-O⁻-3-OH⁻ and 2-OH-3-O⁻-pyridine. Therefore we can draw conclusion that the anion of 2,3-dioxypyridine has a lactam rather than lactim structure.

Table IV and Fig. 4 give the calculation results for dianion of 2,6-dioxypyridine and a correlation diagram for the anions and neutral molecules, respectively. From these results

we can draw the conclusion that the dianion should be rather described by the lactim structure (2,6-diO⁻-pyridine). The calculation results correctly interpret the blue shift of the first band and the red shift of the second band when passing from monoanion to dianion.

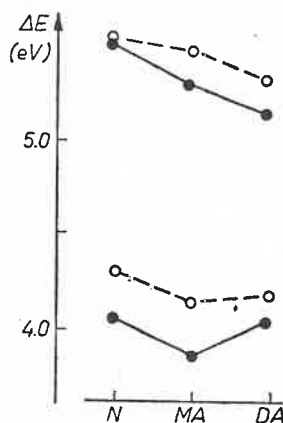


Fig. 4. Neutral (*N*), monoanion (*MA*) and dianion (*DA*) of 2,6-dioxypyridine — comparison between observed (●) and calculated (○) singlet-singlet transition energies

As we see from the results of the present paper and the series of previous ones, the semiempirical Pariser-Parr-Pople type of calculations can be successfully used to interpret π -spectra of different species (neutral, anionic and cationic ones) of oxopyridines indicating the lactim-lactam tautomerism.

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