

Electronic Spectra and Structure of 2-Halocarboxypyridine *N*-Oxides

A. PUSZKO

Department of Organic Chemistry, Academy of Economics, PL-53 345 Wrocław

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UV spectra of 2-halocarboxypyridine *N*-oxides are presented and the influence of substituents on λ_{\max} and ϵ_{\max} of spectral bands is discussed. The electronic spectra were calculated by a modified INDO method. Transition energies, intensities, and assignments were compared with the UV spectra.

Pyridine *N*-oxides are an interesting functional class of organic compounds, since the $N^+—O^-$ group exhibits both π -electron-acceptor and π -electron-donor properties [1]. Of these two effects the latter is known as the so-called back donation [2]. The degree of back donation depends on the substituent(s) in the pyridine ring and can be expressed by the partial π -bond order in the $N^+—O^-$ group. The degree of back donation obtained from ^{17}O nuclear quadrupole resonance spectra is equal to 0.247 (25 %) for pyridine *N*-oxide and 0.312 (31 %) for its 4-nitro derivative [3]. The intramolecular charge transfer, *i.e.* back donation in 3-methyl-4-nitropyridine *N*-oxide was discussed recently [3]. The UV spectra provide the measure of the intramolecular charge transfer in the excited states.

In recent years, the UV spectra of pyridine *N*-oxides were investigated by various scientists [4–9], however, the complex spectroscopic investigations of carboxyl derivatives of pyridine were not done in detail [10], although these compounds are important in the field of organic chemistry and biochemistry. It was interesting to learn how the presence of three substituents (halogen, carboxyl, *N*-oxide group), which have different electronegativity and mesomeric effect and are situated in various positions of pyridine ring, affects the λ_{\max} and ϵ_{\max} of spectral bands.

EXPERIMENTAL

2-Halocarboxypyridine *N*-oxides used in this study were synthesized by the previously described methods [9].

The absorption of title compounds was recorded on a UV VIS (Zeiss, Jena) spectrometer, using a quartz cell of 0.097 cm thickness. Samples concentrations were approximately 10^{-4} mol dm $^{-3}$ in ethanol.

The interpretation of the spectra investigated was carried out by means of a modified INDO method [11]. The ground state geometry of the species was optimized using the semiempirical AM1 method [12].

RESULTS AND DISCUSSION

In the previous paper [5] the author has reported on the effect of halogen, the methyl and nitro group on the absorption spectra of pyridine and pyridine *N*-oxide. In order to obtain the knowledge on the effect of an electron-attracting substituent, the author measured the ultraviolet absorption spectra of isomeric 2-halocarboxypyridine *N*-oxides in ethanol and discussed the effect of a carboxyl group on the spectra of 2-halopyridines and 2-halopyridine *N*-oxides. The absorption of pyridine in ethanol at $\lambda = 256$ nm shifts to the longer wavelength (283.1 nm \rightarrow 293.7 nm) by the introduction of a carboxyl group and halogen to the pyridine ring [6]. On passing from 2-halocarboxypyridines to their *N*-oxides the band II and the band III exhibit a red shift, because the electron migration from the ring to the carboxyl group is facilitated by the $N \rightarrow O$ group acting as an electron-repelling group. *N*-Oxidation of 2-halocarboxypyridine results in a λ -red shift (283.1–293.7 nm \rightarrow 283.2–299.5 nm, 229–251 nm \rightarrow 240–253.5 nm) and in the increase of the relative intensity (4288–12990 \rightarrow 7424–19406, 6224–17094 \rightarrow 16100–20500), which serves as an evidence for the existence of conjugation between a carboxyl and *N*-oxide group.

The experimental positions of bands and their intensities measured in ethanol, together with the theoretical spectra are summarized in Table 1. The positions of the theoretical bands of a remarkable oscillator strength have been matched with the observed experimental ones, which was easy and unambiguous in each case, which in turn indicates that the agreement between theoretical and experimental data is acceptable, regardless to the solvation effect. As it could be expected, the first intense band observed in the spectra of all *N*-oxides has a redox character [4]. It involves mainly the charge transfer from the *N*-oxide oxygen to the ring, though especially in the case of 2-

Table 1. Comparison of the Computed and Experimental Spectra of Halocarboxypyridine *N*-Oxides

Compound	Transition	Pol.	Calculated		Experimental		
			Energy eV	Oscillator strength kN m ⁻¹	Dipole moment 3.356 × 10 ³⁰ C m	Energy eV	{ε} 10 ⁻³
2-Chloro- 3-carboxy- pyridine <i>N</i> -oxide	(π* ← n)	<i>z</i>	3.63	0.000	5.53		
	(π* ← π)	<i>y</i>	4.00	0.134	6.49		
	(π* ← π)	<i>y</i>	4.16	0.175	3.15		
	(π* ← n)	<i>z</i>	4.86	0.001	3.34	4.32	11.97
	(π* ← n)	<i>z</i>	5.62	0.001	8.89	5.14	1.61
	(π* ← π)	<i>x</i>	5.90	0.588	15.52		
	(π* ← π)	<i>y</i>	6.21	0.968	4.78		
	(π* ← n)	<i>z</i>	6.77	0.000	4.29		
	(π* ← n)	<i>z</i>	6.98	0.000	8.57		
	(π* ← π)	<i>x</i>	7.07	0.014	17.94		
					13.00		
2-Chloro- 4-carboxy- pyridine <i>N</i> -oxide	(π* ← π)	<i>x</i>	3.87	0.000	5.87		
	(π* ← π)	<i>y</i>	4.09	0.372	7.67		
	(π* ← π)	<i>x</i>	4.33	0.044	0.72	4.14	7.40
	(π* ← n)	<i>z</i>	5.26	0.001	1.26		
	(π* ← n)	<i>z</i>	5.58	0.000	6.24		
	(π* ← π)	<i>x</i>	5.86	0.580	19.40		
	(π* ← π)	<i>y</i>	6.54	0.963	3.78		
	(π* ← n)	<i>z</i>	6.99	0.000	4.37		
	(π* ← π)	<i>y</i>	7.07	0.012	11.17		
	(π* ← n)	<i>z</i>	7.16	0.000	11.77		
					20.94		
2-Chloro- 6-carboxy- pyridine <i>N</i> -oxide	(π* ← n)	<i>z</i>	3.56	0.000	7.78		
	(π* ← π)	<i>y</i>	4.11	0.204	5.07		
	(π* ← π)	<i>y</i>	4.55	0.041	5.91		
	(π* ← n)	<i>z</i>	4.79	0.001	4.58	4.38	7.42
	(π* ← n)	<i>z</i>	5.26	0.001	8.28		
	(π* ← π)	<i>y</i>	5.72	0.790	5.91	5.05	23.41
	(π* ← π)	<i>y</i>	6.10	0.092	8.12		
	(π* ← n)	<i>z</i>	6.36	0.000	3.40		
	(π* ← π)	<i>y</i>	6.46	0.732	11.82		
	(π* ← π)	<i>y</i>	7.45	0.083	3.78		
					9.70		
2-Bromo- 3-carboxy- pyridine <i>N</i> -oxide	(π* ← n)	<i>z</i>	3.34	0.000	5.02		
	(π* ← π)	<i>x</i>	3.77	0.166	5.21		
	(π* ← π)	<i>y</i>	4.20	0.103	4.03		
	(π* ← n)	<i>z</i>	4.66	0.004	3.56		
	(π* ← n)	<i>z</i>	4.78	0.000	14.54		
	(π* ← n)	<i>z</i>	5.46	0.004	9.48	4.89	19.40
	(π* ← π)	<i>x</i>	5.70	1.022	8.88	5.09	19.80
	(π* ← π)	<i>y</i>	5.82	0.672	13.69		
					5.48		
2-Bromo- 6-carboxy- pyridine <i>N</i> -oxide	(π* ← n)	<i>z</i>	3.36	0.000	7.81		
	(π* ← π)	<i>y</i>	4.01	0.188	4.25		
	(π* ← π)	<i>x</i>	4.34	0.067	4.53		
	(π* ← n)	<i>z</i>	4.83	0.000	5.59	4.27	10.66
	(π* ← n)	<i>z</i>	4.92	0.005	6.04		
	(π* ← n)	<i>z</i>	5.07	0.000	10.00		
	(π* ← π)	<i>x</i>	5.51	0.953	3.83	5.16	20.10
	(π* ← π)	<i>y</i>	5.95	0.464	7.68		
	(π* ← π)	<i>y</i>	6.02	0.375	4.47		
					4.13		

Lack of experimental dipole moment for the reason of insolubility of the title compound in benzene.

chloro-4-carboxypyridine *N*-oxide the substituent also contributes significantly to this charge transfer. The next intense band in all cases considered has mainly the character of pyridine ¹L_a band. It is blue-shifted

when compared with pyridine.

The fact that the band I (near λ = 320 nm) [13] of the title compounds disappears in alcohol as a solvent was the main reason to assign it to a π* ← n

Table 2. The Values of Net Electron Charges at the Atoms and HOMO—LUMO Energies of 2-Halocarboxypyridine *N*-Oxides

Atom	2-Chloro-3-carboxy-pyridine <i>N</i> -oxide			2-Chloro-4-carboxy-pyridine <i>N</i> -oxide			2-Chloro-6-carboxy-pyridine <i>N</i> -oxide			2-Bromo-3-carboxy-pyridine <i>N</i> -oxide			2-Bromo-6-carboxy-pyridine <i>N</i> -oxide		
	S ₀	S ₁	S ₂	S ₀	S ₁	S ₂	S ₀	S ₁	S ₂	S ₀	S ₁	S ₂	S ₀	S ₁	S ₂
N-1	0.473	0.208	0.400	0.518	0.290	0.262	0.433	0.159	0.240	0.498	0.234	0.412	0.459	0.163	0.236
C-2	0.301	0.178	0.319	0.291	0.255	0.300	0.326	0.266	0.360	0.206	0.070	0.039	0.226	0.142	0.163
C-3	-0.114	-0.135	-0.297	-0.092	-0.176	-0.155	-0.076	-0.151	-0.183	-0.079	-0.076	-0.148	-0.033	-0.056	-0.042
C-4	0.035	-0.269	0.009	-0.021	-0.242	-0.130	0.037	-0.204	-0.074	0.024	-0.189	0.057	0.026	0.018	-0.075
C-5	-0.047	-0.122	-0.104	0.028	-0.093	-0.050	-0.035	-0.040	-0.031	-0.032	-0.133	-0.177	-0.019	-0.040	-0.057
C-6	0.088	0.029	-0.189	0.047	-0.004	-0.014	0.051	-0.081	-0.083	0.079	0.058	0.110	0.042	-0.048	0.024
X-7	-0.112	-0.120	-0.070	-0.126	-0.129	-0.072	-0.121	-0.125	-0.073	-0.106	-0.227	-0.208	-0.089	-0.167	-0.103
C-8	0.800	0.794	0.778	0.798	0.715	0.787	0.795	0.766	0.752	0.797	0.797	0.767	0.794	0.772	0.779
O-9	-0.600	-0.604	-0.618	-0.589	-0.655	-0.590	-0.449	-0.398	-0.457	-0.600	-0.597	-0.618	-0.450	-0.396	-0.453
O-10	-0.465	-0.465	-0.470	-0.461	-0.474	-0.463	-0.595	-0.619	-0.630	-0.442	-0.442	-0.447	-0.595	-0.612	-0.587
H-11	0.037	0.037	0.037	0.028	0.030	0.028	0.039	0.042	0.039	0.016	0.017	0.016	0.038	0.041	0.038
O-12	-0.727	0.137	-0.123	-0.705	0.141	-0.242	-0.737	0.051	-0.191	-0.709	0.138	-0.151	-0.724	0.053	-0.247
HOMO/eV		-10.69			-10.67			-11.27			-10.67			-11.28	
LUMO/eV		-2.02			-2.20			-2.37			-2.18			-2.37	
HOMO—LUMO/eV		-8.67			-8.47			-8.90			-8.49			-8.91	

transition. The band II has a nature of intramolecular charge transfer ($\lambda = 283.2\text{--}299.5$ nm) from the oxygen atom of the $\text{N}^+\text{--O}^-$ bond to the ring and so the intramolecular charge transition occurs from the oxygen atom of *N*-oxide group to the ring residue and symmetry $^1\text{A}_1$. Accordingly the band II may be affected more by the perturbation at the *para* position (see 2-chloro-4-carboxypyridine *N*-oxide). The red shift of bands II and III ($\lambda = 240.0\text{--}253.5$ nm) in relation to pyridine *N*-oxide caused by halogen and carboxyl group is sensitive not only to the position of the carboxyl group in relation to the *N*-oxide group, but also to that of halogen. The transition from the ground state to the excited one is connected with charge density changes in the molecule (Table 2). Similarly to pyridine *N*-oxide, 2-halocarboxypyridine *N*-oxides in the ground state are also loaded with the highest negative charge at the oxygen atom of the *N*-oxide group. Its highest value appears to be observed at the *N*-oxide group with a carboxyl group attached to the position 6. 2-Chloro-4-carboxypyridine *N*-oxides are loaded with the smallest negative charge at the oxygen of the *N*-oxide group, but its value appears to be the lowest among all of these compounds examined for the purpose of this work. In the case of 2-chloro-4-carboxypyridine *N*-oxide the charge transfer from *N*-oxide group to the ring group appears to be the highest. The positive charge at the position 2 in the title compound should influence the reactivity of 2-halocarboxypyridine *N*-oxides with nucleophilic reagents.

2-Chlorocarboxypyridine *N*-oxides, like pyridine *N*-oxide, compared to its ground state, exhibit a lower negative charge at the position 4 of the pyridine ring. On transition from the ground state to the first excited state in 2-halocarboxypyridine *N*-oxide, the value of the negative charge at the oxygen atom of the *N*-oxide group is lowered and increased at the position 4. The above observations, as well as the increase of negative charge at the carbon atom in the positions 3 and 5 in the first excited state, appear to indicate that the intramolecular charge transition occurs from the oxygen atom of *N*-oxide group to the ring. Among all of 2-halocarboxypyridine *N*-oxides the degree of the above-mentioned intramolecular transfer is the highest in 6-carboxyl derivatives.

Difference values of the HOMO—LUMO energies oscillate for examined compounds from -8.91 to -8.47 eV and are smaller than those for 2-halopicoline *N*-oxides ($-9.31\text{--}9.35$ eV) and pyridine *N*-oxide (8.97 eV). These facts should point out the higher susceptibility of photochemical reactions in comparison with 2-halopyridine *N*-oxides and pyridine *N*-oxides.

The values of HOMO energies of 2-halocarboxypyridine *N*-oxides allow to predict the order (r) of reactivity of nucleophilic substitution: $r(2\text{-bromo-6-carboxypyridine } N\text{-oxide}) \geq r(2\text{-chloro-6-carboxypyridine } N\text{-oxide}) > r(2\text{-chloro-3-carboxypyridine } N\text{-oxide}) > r(2\text{-chloro-4-carboxypyridine } N\text{-oxide}) = r(2\text{-bromo-3-carboxypyridine } N\text{-oxide})$. The values of LUMO energies (E) on electrophilic substitution are as follows: $E(2\text{-chloro-3-carboxypyridine } N\text{-oxide}) > E(2\text{-bromo-3-carboxypyridine } N\text{-oxide}) > E(2\text{-chloro-4-carboxypyridine } N\text{-oxide}) > E(2\text{-bromo-6-carboxypyridine } N\text{-oxide}) = E(2\text{-chloro-6-carboxypyridine } N\text{-oxide})$.

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