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ELECTRONIC SPECTRA OF THE ANION RADICALS OF PYRIDINE AND QUINOLINE N-OXIDES

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The electronic spectra of the anion radicals of pyridine and quinoline N-oxides were newly recorded. The radicals were generated by γ-irradiation of the frozen solutions at 77°K. The spectra were interpreted by means of the semiempirical SCFMO-CI calculations.

In a foregoing paper$^{1)}$, we recorded the electronic spectra of the anion radicals of various heterocyclic amine N-oxides and the related N-heterocycles, and discussed systematically and theoretically on the basis of the restricted Longuet-Higgins-Pople type (LP-) open shell SCFMO-CI calculation. The radical generation was made using electrolysis technique in DMF solvent at room temperature.$^{1)}$ The electronic spectra of the anion radicals of pyridine N-oxide ($\mathrm{PNO}^{\dot{-}}$) and quinoline N-oxide ($\mathrm{QNO}^{\dot{-}}$), however, could not be obtained because the radicals are not very stable at room temperature.$^{2)}$ Since $\mathrm{PNO}^{\dot{-}}$ and $\mathrm{QNO}^{\dot{-}}$ are important basic radicals among many heterocyclic N-oxide anion radicals, we have here examined the spectra at lower temperature. The anion radicals were obtained by γ-ray irradiation technique. This method, which is fairly familiarized by now for the selective production of various ion-radicals,$^{3,4)}$ is capable of yielding the anion radicals by the coupled reactions below.

$$\text{MTHF (major constituent in the solution)} \xrightarrow{\gamma\text{-ray}} \mathrm{MTHF}^{\dot{+}} + e^-$$

$$e^- + \text{N-oxide (minor constituent)} \longrightarrow \text{N-oxide}^{\dot{-}},$$

where MTHF stands for 2-methyltetrahydrofuran. Details of the method are described elsewhere.$^{3,4)}$ The observed electronic spectra of the anion-radicals of PNO and QNO are demonstrated in Fig.'s 1 and 2, respectively. Since PNO is sparingly soluble in MTHF at 77°K, the spectral measurement of the anion radical was less straightforward. The transition energies, oscillator strengths, and polarizations of $\mathrm{PNO}^{\dot{-}}$ and $\mathrm{QNO}^{\dot{-}}$ were already calculated in π-electron approximation based on the LP-SCFMO-CI method.$^{1)}$ Here we have also recalculated the excited states of $\mathrm{PNO}^{\dot{-}}$ and $\mathrm{QNO}^{\dot{-}}$ by applying the open shell CNDO/S procedure.$^{5)}$ Almost the same results were obtained by the above two kinds of calculations for $\mathrm{PNO}^{\dot{-}}$ and $\mathrm{QNO}^{\dot{-}}$. All the calculated and observed results are given in Table 1. The spectra shown in Fig.'s 1 and 2 may be due to the π-π^* transitions. For the observed bands at 2.44 eV of $\mathrm{QNO}^{\dot{-}}$ and at ~3.30 eV (sh) of $\mathrm{PNO}^{\dot{-}}$, the calculated results obtained by LP-SCFMO-CI for the former and CNDO/S for the latter may be more likely from the viewpoint of f values, as is seen in Table 1. The failure of the detection of $1\ {}^2A_2$ state of $\mathrm{PNO}^{\dot{-}}$ may be justified by the predicted low transition energy and the extreme weakness of the intensity.

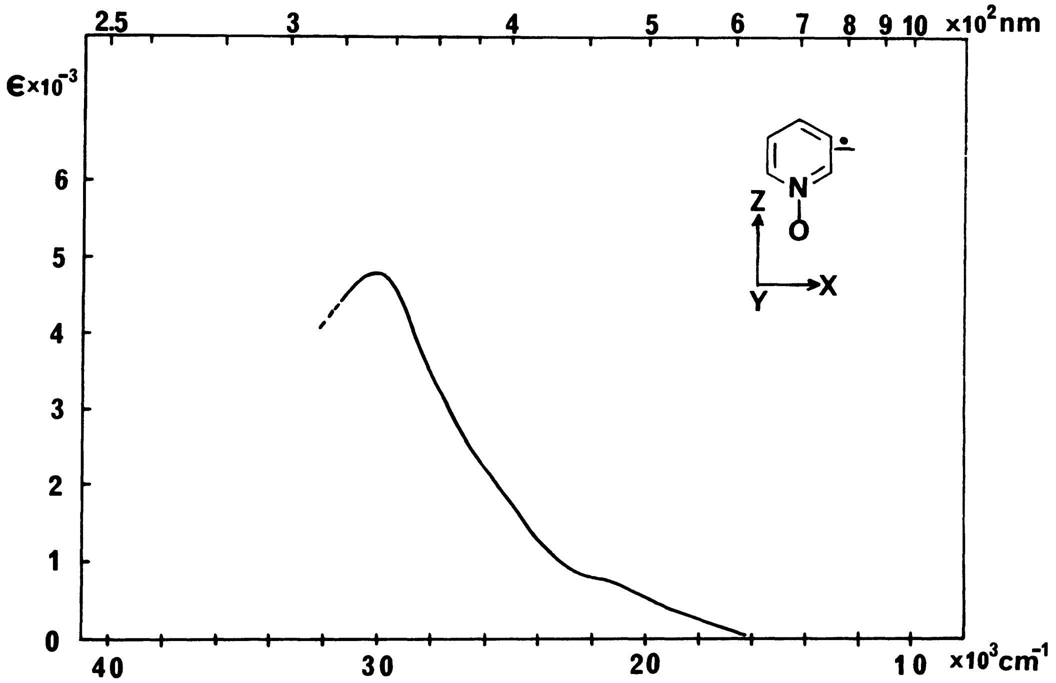

Fig. 1. Electronic spectrum of pyridine N-oxide anion radical. The coordinate given in this figure is employed for the excited state calculation shown in Table 1.

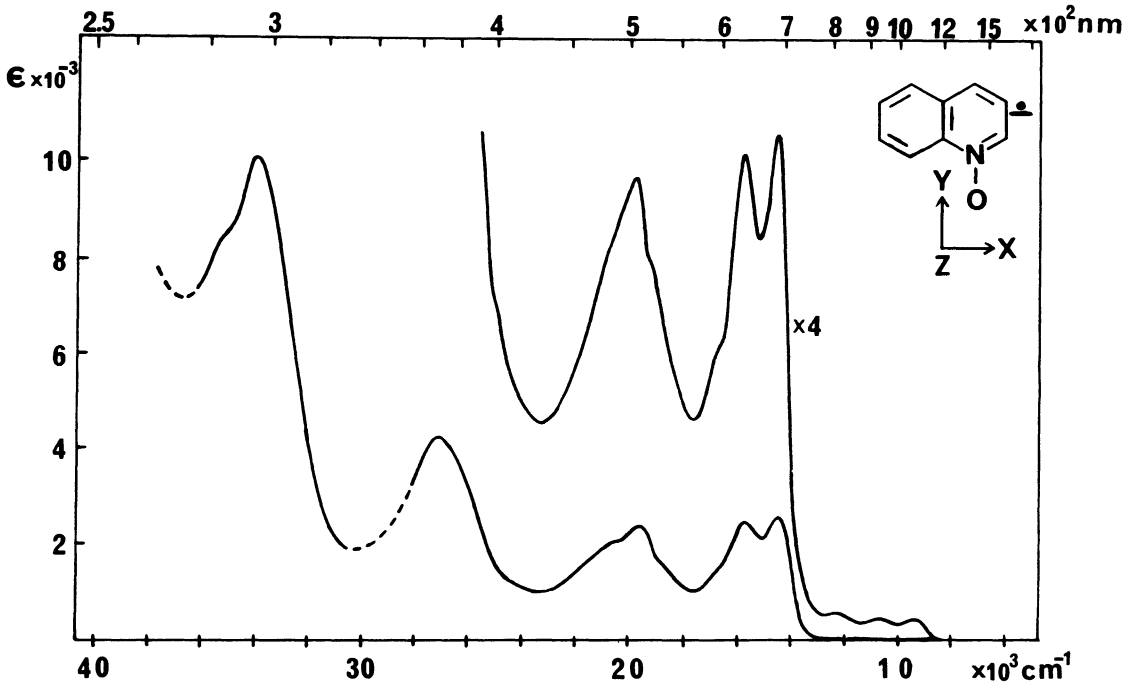

Fig. 2. Electronic spectrum of quinoline N-oxide anion radical. The coordinate given in this figure is employed for the excited state calculation shown in Table 1.

Table 1. Calculated Transition Energies (eV), Oscillator Strengths (f values) and Polarizations, Observed Energies (eV) and Intensities (ε Values), and Band Assignment of the Anion Radicals Given

Anion	LP-SCFMO-CI a,c)				CNDO/S b,c)				Observed values	
Radicals	ΔE (eV)	f	$^2\Gamma$	P	ΔE (eV)	f	$^2\Gamma$	P	ΔE (eV)	ε
PNO d)	0.00	--	$^2B_2$ e)		0.00	--	$^2B_2$ e)			
	0.35	0.000	$^2A_2$	X	0.36	0.001	$^2A_2$	X	--	--
	2.46	0.020	$^2B_2$	Z	2.23	0.015	$^2B_2$	Z	2.67	760
	3.27	0.121	$^2B_2$	Z	3.70	0.058	$^2B_2$	Z	~3.30(sh) f)	~2500
	--	--	--	--	3.83	0.000	$^2B_1$	--	--	--
	3.81	0.108	$^2A_2$	X	4.27	0.096	$^2A_2$	X	3.72	4800
	5.38	0.036	$^2B_2$	Z	5.34	0.064	$^2A_2$	X		
	5.53	0.048	$^2A_2$	X	5.72	0.029	$^2B_2$	Z		
QNO d)	0.00	--	$^2A''$ e)		0.00	--	$^2A''$ e)			
	1.29	0.001	$^2A''$	X, Y	1.54	0.004	$^2A''$	X, Y	1.16 1.33 1.55	125 125 145
	1.90	0.054	$^2A''$	X, Y	1.66	0.020	$^2A''$	X, Y	1.80 1.95	2580 2500
	2.17	0.060	$^2A''$	X, Y	2.39	0.003	$^2A''$	X, Y	2.44	2400
	2.90	0.120	$^2A''$	X, Y	3.16	0.104	$^2A''$	X, Y	3.37	4250
	--	--	--	--	3.50	0.000	$^2A'$	Z	--	--
	3.53	0.027	$^2A''$	X, Y	3.69	0.006	$^2A''$	X, Y		
	3.64	0.231	$^2A''$	X, Y	4.04	0.102	$^2A''$	X, Y	4.21	10040
	4.64	0.003	$^2A''$	X, Y	4.82	0.030	$^2A''$	X, Y		
	4.80	0.154	$^2A''$	X, Y	4.95	0.186	$^2A''$	X, Y		
	4.95	0.038	$^2A''$	X, Y	5.24	0.007	$^2A''$	X, Y		

a) The calculated data for this π-π approximation were cited from reference 1. b) See reference 5. The σ-π separation parameter is 0.585, and the type of a quadratic equation is employed for estimating the two-electron repulsion terms. It is adopted that the N→O bond distance is 1.29 Å and the regular hexagon with the distance of 1.40 Å is assumed for ring systems. c) Main configurations entering into CI are similar between LP-SCFMO-CI and CNDO/S calculations. Also πMO's obtained by LP-SCFMO and CNDO/S are quite similar to each other except only that for QNO$^{\dot{-}}$ the vacant πMO's 29 and 30 obtained by CNDO/S have more or less the form of the linear combination of vacant πMO's 8 and 9 led from the LP-SCFMO, such as $\psi_{29(30)} = a\psi_8 +$ (or -) $b\psi_9$. Note that the half-filled MO of QNO$^{\dot{-}}$ is ψ_7 and ψ_{28} for LP-SCFMO and CNDO/S, respectively. d) The coordinates used are given in Fig.'s 1 and 2. e) These are species for ground state. f) This indicates shoulder bands.

It is noteworthy that the theoretical prediction made in the previous study[1] for the series of PNO, QNO, and acridine N-oxide anion radicals has been substantiated by the present work.[6]

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