Electronic Spectra and Structures of Organic π-Systems. IV. Electronic Spectra of Nitropyrroles

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The electronic spectra of 2-nitropyrrole and 3-nitropyrrole have been measured in various solvents and compared with the values calculated by the variable integrals method II. Agreement between the observed and the calculated transition energies is satisfactory. From eigenvectors of both nitropyrroles, the localization of molecular orbitals to the moiety of molecule has been discussed. The π-electon densities and π-bond orders of both molecules have also been calculated.

We have proposed a new type of modified Pariser-Parr-Pople method, the variable integrals method II, which contains no arbitrary adjusting parameters and needs no guess work in estimating a set of suitable parameters to calculate the electronic spectra of the molecule in question. The method was applied to various kinds of molecules with great success.[1,2]

The electronic spectra of 2-nitropyrrole and 3-nitropyrrole were measured in various solvents and the results were compared with the calculated values.

Experimental

Materials. Nitration of pyrrole was carried out according to Rinkes[3] and needle crystals with mp 60—62°C were obtained. They were dissolved in a benzene-ether (1 : 1) mixture and chromatographed on a silica gel column. Elutions gave substance (I), mp 65°C, as golden yellow coloured needles from carbon tetrachloride (Found: C, 43.03; H, 3.30; N, 24.98; O, 28.42%. Calcd for $C_4H_4N_2O_2$: C, 42.86; H, 3.59; N, 24.99; O, 28.56%, and substance (II), mp 101—102°C, from benzene as yellow crystals (Found: C, 43.02; H, 3.86; N, 25.01; O, 28.60%. Calcd for $C_4H_4N_2O_2$: C, 42.86; H, 3.59; N, 24.99; O, 28.56%). The mass spectrum of each compound showed a parent peak of $m/e=112$. The compounds were identified as monomers of nitropyrroles. There has been some confliction[3-5] concerning the structural identification of nitropyrroles. For instance Safonova and coworkers[4] have reported the mp of 2-nitropyrrole as 55°C and that of 3-isomer to be 64°C. The substance with mp 101°C obtained by the decarboxylation of 4-nitropyrrole-2-carboxylic acid was regarded as a dimer of nitropyrrole.[5] On the other hand, Morgan and Morrey[6] reported that the substances with mp 65—66°C and mp 99—101°C are 2-nitropyrrole and 3-isomer, respectively, and the substance with mp 63—64°C is a mixture of two isomers.

In order to investigate molecular electronic spectra, there should be no ambiguity about the position of the substituent. Thus we confirmed the position of nitro-group by the following infrared method. The infrared spectra of nitropyrroles I and II were measured in carbon tetrachloride on a JASCO DS-402G spectrophotometer. Nitropyrrole I shows three peaks in the NH stretching region at a high concentration. The three peaks at 3470 cm^{-1}, 3390 cm^{-1}, and 3265 cm^{-1} are assigned to the free ν_{N-H}, the intramolecular hydrogen bonded ν_{N-H}, and the intermolecular hydrogen bonded ν_{N-H}, respectively. The peak at 3265 cm^{-1} disappears on dilution. On the other hand, nitropyrrole II shows two peaks in the NH stretching region. The two peaks at 3493 cm^{-1} and 3385 cm^{-1} are regarded as the free and the intermolecular hydrogen bonded N-H stretching vibrations,

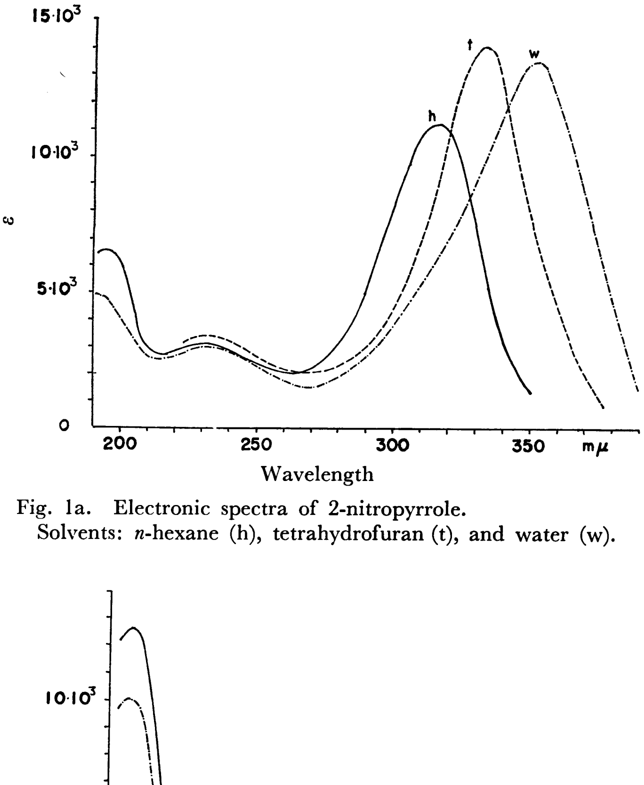

Fig. 1a. Electronic spectra of 2-nitropyrrole.
Solvents: *n*-hexane (h), tetrahydrofuran (t), and water (w).

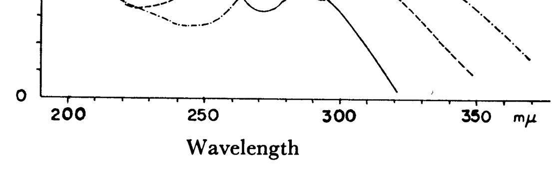

Fig. 1b. Electronic spectra of 3-nitropyrrole.
Solvents: *n*-hexane (h), tetrahydrofuran (t), and water (w).

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4) E. N. Safonova, V. M. Belikov, and S. S. Novikov, *Izvest. Akad. Nauk* S. S. S. R. Otdel. Khim. Nauk, 1307 (1959).

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TABLE 1. THE MAXIMUM WAVELENGTHS (mμ) AND MOLAR EXTINCTION COEFFICIENTS (IN PARENTHESES) OF NITROPYRROLES IN VARIOUS SOLVENTS

Solvent				
		2-Nitropyrrole		
n-Hexane	193.5 (6590),	230.5 (3090),		315.5 (11190)
Tetrahydrofuran		230 (3400),		332.5 (14020)
Acetonitrile		231 (2930),		335 (12770)
Methanol		230 (3390),		336 (13010)
Water		232.5 (2940),		351.5 (13480)
		3-Nitropyrrole		
n-Hexane	198.5 (12660),		246 (6280),	286.5 (3940)
Tetrahydrofuran		222^{sh} (3380),	265 (6110),	309.5 (4330)
Acetonitrile	202 (10870),	224 (3470),	267.5 (6530),	313.5 (4470)
Methanol		222 (3570),	269 (6330),	313 (4510)
Water	198 (10800),	222.5^{sh} (3400),	281 (6200),	329 (4410)

TABLE 2. SCF EIGENVALUES AND EIGENVECTORS FOR 2-NITROPYRROLE AND 3-NITROPYRROLE

Ψ_i	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	E_i (eV)
2-Nitropyrrole									
1	0.3994	0.4117	0.1808	0.1032	0.1576	0.5937	0.3543	0.3534	−17.9963
2	0.6687	0.1817	0.1321	0.1957	0.3594	−0.3694	−0.3177	−0.3128	−16.3802
3	−0.4282	0.1922	0.5252	0.4608	0.1038	−0.0191	0.2870	−0.4450	−12.7252
4	0.2635	−0.1310	−0.3132	−0.2718	−0.0500	−0.0054	0.6668	−0.5425	−12.6115
5	−0.0309	−0.5716	−0.2300	0.4414	0.5722	−0.0035	0.2054	0.2345	−11.6450
6	−0.2307	0.2068	−0.4358	−0.0164	0.3410	0.5305	−0.3839	−0.4107	−2.0095
7	0.2922	−0.4280	0.0736	0.4242	−0.5442	0.4005	−0.2060	−0.2168	0.5868
8	0.0320	−0.4367	0.5727	−0.5383	0.3048	0.2625	−0.1208	−0.1190	1.6233
3-Nitropyrrole									
1	0.3483	0.2810	0.3675	0.1774	0.1819	0.5822	0.3614	0.3612	−17.5224
2	0.7039	0.2901	0.0286	0.1345	0.3226	−0.3662	−0.2898	−0.2818	−16.5309
3	−0.4750	0.1666	0.5888	0.5142	0.1208	−0.0641	−0.2657	−0.2151	−12.5753
4	−0.0138	−0.0432	−0.0018	0.0612	0.0552	−0.0096	0.7069	−0.7010	−12.3557
5	−0.0320	−0.5478	−0.3013	0.4531	0.6068	0.0020	0.0547	0.1776	−11.5936
6	0.2210	−0.5046	0.2080	−0.1609	−0.0683	0.5484	−0.3992	−0.4033	−1.5166
7	0.3274	−0.3750	0.1956	0.4544	−0.6221	−0.2718	0.1468	0.1586	0.2666
8	−0.0202	0.3346	−0.5875	0.4946	−0.2921	0.3848	−0.1769	−0.1822	1.8670

respectively. The peak at 3385 cm^{-1} disappears on dilution. Thus it was concluded that nitropyrrole I is 2-nitropyrrole and nitropyrrole II 3-isomer.

Measurements. Ultraviolet and visible spectra were obtained with a Hitachi Model EPS-3T spectrophotometer, in *n*-hexane, tetrahydrofuran, acetonitrile, methanol, and water.

Results. The ultraviolet and visible absorption spectra of the compounds in several solvents are shown in Fig. 1. The peak wavelengths of these spectra are summarized in Table 1. Morgan and Morrey[6] have reported the λ_{max} and ε_{max} of these compounds observed in *n*-hexane and methanol. They are consistent with our results, although the spectra around 200 mμ have not been measured.

Theoretical

Method. The variable integrals method II was used.[1,2] The molecular structures of nitropyrroles are assumed as shown in Fig. 2 using the structural data of pyrrole[7] and *p*-nitroaniline.[8] Numberings of the atomic orbitals are also given in Fig. 2.

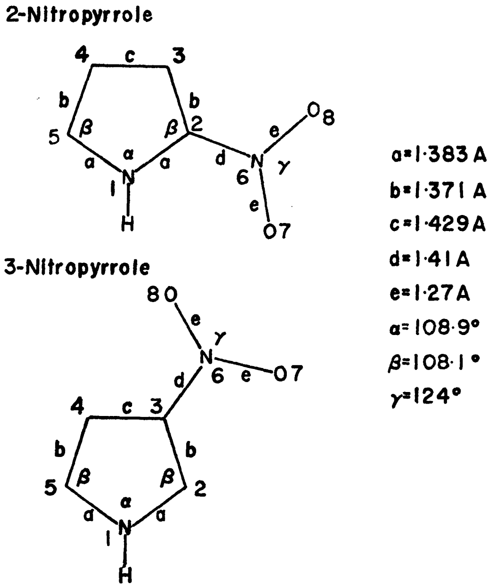

Fig. 2. Assumed structures of nitropyrroles.

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[7] B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).

[8] J. Donohue and K. N. Trueblood, *Acta Crystallogr.*, **9**, 960 (1956).

Results and Discussion

The SCF eigenvalues and eigenvectors of nitropyrroles are shown in Table 2. The molecular orbitals ϕ_5 and ϕ_8 of 2-nitropyrrole, and ϕ_3, ϕ_5, and ϕ_7 of 3-nitropyrrole are mainly localized on pyrrole ring, and the molecular orbitals ϕ_4's of both nitropyrroles are almost localized in nitro-groups. The other molecular orbitals are delocalized over both pyrrole and nitro-groups.

The π-electron densities and bond orders are summarized in Table 3. In the ground state the charges of about −0.11 *e* and −0.09 *e* are transferred from pyrrole group to nitro-group in 2- and 3-nitropyrroles, respectively.

TABLE 3. π-ELECTRON DENSITIES AND BOND ORDERS

	2-Nitropyrrole	3-Nitropyrrole
Electron densities		
1	1.7207	1.6871
2	1.1667	0.9857
3	0.9534	1.1467
4	1.0599	1.0461
5	0.9892	1.0461
6	0.9785	0.9546
7	1.5913	1.5757
8	1.5403	1.5581
Bond orders		
1—2	0.3735	0.4821
1—5	0.4560	0.4257
2—3	0.7434	0.7497
3—4	0.5399	0.4704
4—5	0.8010	0.8322
2—6	0.3527	
3—6		0.3304
6—7	0.6357	0.6538
6—8	0.6719	0.6687

The calculated transition energies are summarized in Table 4 with the observed ones in *n*-hexane.

TABLE 4. CALCULATED π-$^1\pi^*$ TRANSITION ENERGIES IN eV

E	*f*	CI Composition[a]		$E_{\text{obsd.}}$	$\varepsilon_{\text{obsd.}}$
2-Nitropyrrole					
4.327	0.525	5—6	0.941	3.93	11190
4.729	0.162	3—6	0.736		
		4—6	0.551		
		4—7	0.324		
5.354	0.303	3—6	−0.520	5.39	3090
		4—6	0.747		
		5—8	0.344		
6.457	0.032	5—7	0.938	6.41	6590
7.252	0.096				
3-Nitropyrrole					
4.658	0.077	4—6	0.644	4.34	3940
		5—6	0.659		
4.962	0.429	4—6	−0.653	5.04	6280
		5—6	0.511		
		3—6	−0.418		
5.252	0.265	3—6	0.833	5.58$^{\text{sh}}$	3380[b]
		5—6	0.423		
6.136	0.397	5—7	0.931	6.25	12660
6.965	0.159				

The observed values are those in *n*-hexane.

a) The transition denoted by *i*-*j* refers to a one-electron excitation from orbital *i* to virtual orbital *j*. The second column gives the CI coefficient of the configuration *i*-*j*.

b) Observed values in tetrahydrofuran.

In the case of 2-nitropyrrole the calculated 5.354 eV and 6.457 eV transitions are in good agreement with the observed values. From the CI coefficients we see that the 4.327 eV transition is the so-called intramolecular chage-transfer transition associated with electron migration from pyrrole group to nitro-group. This is consistent with the observed large solvent effect on the longest wavelength band. The 4.729 eV transition is contributed from a charge-transfer configuration, a local excitation configuration in nitro-group and a back charge-transfer configuration associated with electron transfer from nitro-group to pyrrole group. The corresponding band seems to be hidden by the other stronger bands. The 5.354 eV transition is contributed from a charge-transfer configuration, a local excitation configuration in nitro-group and a local excitation configuration in pyrrole group. The 6.457 eV transition is mainly contributed from a localized excitation configuration in pyrrole group.

In the case of 3-nitropyrrole the caluclated transition energies are in good agreement with the observed values. The calculated 5.252 eV transition has the character of the so-called intramolecular charge-transfer transition associated with electron migration from pyrrole group to nitro-group. The 4.658 eV and the 4.962 eV transitions are the transitions contributed from charge transfer configurations and back charge-transfer configurations. The 6.136 eV band is the local transition in pyrrole ring. In line with this theoretical interpretation, the corresponding observed band showed no appreciable solvent shift.

In conclusion we found that the variable integrals method II is useful for the systems treated in this paper.

The calculation was carried out on a HITAC 5020 E computer at the Computer Centre of the University of Tokyo.